

GERAGHTY & MILLER, INC.

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DEC 17 1987

3.0 QUALITY ASSURANCE PROJECT PLAN

PHASE I REMEDIAL INVESTIGATION
ORMET CORPORATION
HANNIBAL, OHIO

REVISION 3
DECEMBER 11, 1987

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TABLE OF CONTENTS

<u>SECTION</u>	<u>PAGE</u>
3.0 <u>QUALITY ASSURANCE PROJECT PLAN</u>	
3.1 INTRODUCTION	3.1-1
3.2 PROJECT DESCRIPTION	3.2-1
3.3 PROJECT ORGANIZATION AND RESPONSIBILITY	3.3-1
3.3.1 Project Personnel	3.3-1
3.3.2 Field Organization	3.3-3
3.4 QUALITY ASSURANCE OBJECTIVES	3.4-1
3.4.1 Precision	3.4-2
3.4.2 Accuracy	3.4-3
3.4.3 Completeness	3.4-3
3.4.4 Representativeness	3.4-3
3.4.5 Comparability	3.4-4
3.5 DATA AND RECORDS MANAGEMENT	3.5-1
3.5.1 Introduction	3.5-1
3.5.2 Organization	3.5-1
3.5.3 Receipt of Data and Reports	3.5-2
3.5.4 Outgoing Data and Reports	3.5-3
3.5.5 Telephone and Meeting Notes	3.5-3
3.5.6 Document Filing and Access	3.5-4
3.5.7 Computer Data Storage	3.5-4
3.6 SAMPLING PROCEDURES	3.6-1
3.6.1 Drilling and Monitor-Well Installation	3.6-1
3.6.1.1 Soil Boring Procedures	3.6-2
3.6.1.2 Monitor-Well Installation/ Construction/Development Procedures	3.6-6
3.6.1.3 Decontamination of Drilling Rig and Drilling Equipment	3.6-12
3.6.2 Disposal Pond Sampling Procedures	3.6-13
3.6.3 Carbon Runoff Area Sampling/ Boring Procedures	3.6-18
3.6.4 River Sediment Sampling Procedures	3.6-21
3.6.5 Ground-Water Sampling Procedures	3.6-23
3.6.6 Procedures for Collecting and Packaging Seep Samples	3.6-35
3.6.7 Air Monitoring Procedures	3.6-37

DEC 18 1987

TABLE OF CONTENTS (CON'T)

<u>SECTION</u>	<u>PAGE</u>
3.7 SAMPLE CUSTODY	3.7-1
3.7.1 Sample Container Inventory	3.7-1
3.7.2 Field Custody	3.7-2
3.7.3 Transfer of Custody and Shipment	3.7-3
3.7.4 Laboratory Custody	3.7-4
3.7.5 Final Evidence File	3.7-5
3.8 CALIBRATION PROCEDURES AND FREQUENCY	3.8-1
3.9 ANALYTICAL SERVICE	3.9-1
3.9.1 Standard Operating Procedures Quality Assurance Program for Kemron Environmental Services	3.9-2
3.9.2 Contract Laboratory Program Statement of Work for CompuChem Laboratories	3.9-2
3.10 QUALITY CONTROL PROCEDURES	3.10-1
3.10.1 Laboratory Quality Control Checks	3.10-1
3.10.2 Field Quality Control Checks	3.10-1
3.11 PERFORMANCE AND SYSTEMS AUDITS	3.11-1
3.12 PREVENTIVE MAINTENANCE	3.12-1
3.13 SPECIFIC ROUTINE PROCEDURES USED TO ASSESS DATA PRECISION, ACCURACY AND COMPLETENESS	3.13-1
3.14 CORRECTIVE ACTION	3.14-1
3.15 QA REPORTS TO MANAGEMENT	3.15-1

LIST OF QAPP REFERENCES

- REFERENCE 1 - ASTM METHOD D3385-75: STANDARD TEST METHOD
FOR INFILTRATION RATE OF SOILS IN FIELD
USING DOUBLE-RING INFILTROMETERS
- REFERENCE 2 - ASTM METHOD D1586-84: STANDARD METHOD FOR
PENETRATION TEST AND SPLIT BARREL SAMPLING
OF SOILS

LIST OF QAPP REFERENCES (CON'T)

- REFERENCE 3 - METHOD FOR FIELD DESCRIPTION OF SOIL SAMPLES
DESCRIPTION AND IDENTIFICATION OF SOILS
- REFERENCE 4 - CALIBRATION AND MAINTENANCE PROCEDURES FOR
FIELD EQUIPMENT
- REFERENCE 4-A - Calibration of MSA Samplair Pump
- REFERENCE 4-B - Calibration, Maintenance and Operation
of Model OVA-128 Portable Organic
Vapor Analyzer
- REFERENCE 4-C - Calibration of Mini-pH Meter
- REFERENCE 4-D - Calibration of YSI Model 33 s-c-t
- REFERENCE 5 - FIELD PRETREATMENT PROCEDURES FOR REMOVAL
OF SULFIDES AND OXIDIZING AGENTS IN AQUEOUS
SAMPLES COLLECTED FOR CYANIDE ANALYSES
- REFERENCE 6 - AIR MONITORING OPERATIONS AND QUALITY
ASSURANCE PROCEDURES MANUAL FOR ORMET SITE

3.2 PROJECT DESCRIPTION

This Remedial Investigation (RI) is being performed to generate additional environmental quality data to determine the nature and extent of any release or threatened release of hazardous substances, pollutants, or contaminants from the Ormet facility. The Phase I RI includes a variety of investigative activities intended to provide a physical and/or chemical characterization of the potential source areas and affected media at the site. These activities address nine general areas:

♦ Ground Water

Sampling of up to 55 ground-water monitoring wells will be performed. All wells will be analyzed for an extensive list of common water quality parameters and major cations and anions, with selected wells also being analyzed for the organic parameters of the U.S. EPA CLP List.

♦ Former Potliner Storage Area

Soil borings shall be performed at 24 locations within the former potliner storage area, with soil samples being submitted for chemical analysis.

♦ Disposal Ponds

Samples will be collected from several designated depths at numerous horizontal locations within each of the old retention ponds. Composite samples will be submitted for chemical analysis. In addition, permeability testing will be performed on each of the pond surfaces and soil borings will be performed around the perimeter of each pond to characterize the underlying soils.

♦ Ohio River Sediments

Sediment samples will be collected from six locations along the river/plant boundary and submitted for laboratory analysis.

♦ Carbon Runoff and Deposition Area

Samples will be collected from three areas of carbon deposition and also from the soils beneath each area and submitted for laboratory analysis. Also, shallow soil samples will be taken and described over a systematic grid in the area where carbon deposits are located so that the lateral extent of the deposits can be determined.

♦ Construction Material Scrap Dump

Two seeps that emanate from the base of the scrap dump will be sampled and analyzed to assess the quality of the leachate.

♦ Plant Recreation Area Fill

The nature of an area of fill that was identified adjacent to the baseball field will be evaluated by sampling and analyzing two seeps that emanate from near the base of the filled area and also by performing soil borings in the area.

♦ Pond 5 Conduit

A steel conduit extending from the southeastern berm of Pond 5 shall be sampled to determine the quality of the effluent, if water is flowing from it at the time of sampling.

♦ Air Monitoring

High volume air samplers will be used at four locations to determine the amount of respirable dust, if any, that may be carried away from the former potliner storage area and the retention ponds by the wind. Samples will be collected periodically over a term of 10 months.

QUALITY ASSURANCE PLAN

GERAGHTY & MILLER, INC. DEC 18 1987

ENVIRONMENT SERVICES COMPANY

Section No. 3.2
Revision No. 3
Date: 12-11-87
Page 4 of 5

. A substantial quantity of background information and data has been generated through previous investigations conducted at the site. A summary of the background information is presented throughout Section 1 of this Plan and additional data is supplied in Appendices A through D.

A description of the site monitoring (sampling) network and the rationale for its design is provided in Section 2, Site Investigation. The data generated through the sampling network will be used to evaluate any actual or potential threat to human health, welfare or the environment. These data will also be used to determine if remedial actions are required and, if necessary, to facilitate screening of possible remedial technologies and alternatives and to develop a cost-effective and technically manageable remedial system for the site.

A summary of the RI Tasks and objectives is provided in Table 3.2-1 and a matrix of field-data collection activities is provided in Table 3.2-2. A listing of the sampling events, with the number of samples to be generated by each and the corresponding types of analyses is provided in Table 3.2-3. In Table 3.2-4, the detection limits for each of the analytical parameters are given. The anticipated schedule for completion of the Phase I data-collection activities is shown in Figure 3.2-1. These field activities will begin upon approval of the Phase I Work Plan by U.S. EPA and OEPA.

GERAGHTY & MILLER, INC.

DEC 18 1987

ENVIRONMENTAL SERVICES COMPANY

Section No. 3.2
Revision No. 3
Date: 12-11-87
Page 5 of 5

Detailed descriptions of the procedures and protocols for conducting the various data-collection tasks of this investigation are presented throughout the following sections of this QAPP. Samples collected for analyses of non-CLP inorganic parameters, as well as organic parameters of the U.S. EPA CLP List will be analyzed by Kemron Environmental Services (Kemron), Marietta, Ohio. Analyses for the inorganic parameters of the U.S. EPA CLP List will be conducted by CompuChem Laboratories, Inc. (CompuChem), Research Triangle Park, North Carolina. The QA/QC Programs for both Kemron and Compuchem are provided in Section 3.9 to this QAPP.

Kemron will be following the procedures required in the CLP Protocol for the tentative identification of unknown compounds. The details are found in Statement of Work Organic Analysis (Multi-media, Multi-Concentration), USEPA Contract Laboratory Program, 10/86, Page A-4, Task V.

The air monitoring program will be performed by Energy and Environmental Management, Inc. of Murrysville, Pennsylvania. The air filters will be sent to Hazen Research, Inc. in Golden, Colorado for weighing.

TABLE 3.2-1
SUMMARY OF REMEDIAL INVESTIGATION
TASKS AND OBJECTIVES

TASK BREAKDOWN	OBJECTIVES
Work Plan Preparation <ul style="list-style-type: none"> ■ Health and Safety ■ Sampling and Analysis ■ QA/QC 	<ul style="list-style-type: none"> ■ Fulfill EPA and OEPA requirements for RI ■ Ensure representativeness and accuracy of data collected during the RI
<hr/>	
Additional Monitoring Wells <ul style="list-style-type: none"> ■ West of Pond 3 ■ ±200' south of MW-12 ■ Southeast of TH-3 	<ul style="list-style-type: none"> ■ Provide additional ground-water monitoring data specifically requested by EPA and OEPA
<hr/>	
Ground-Water Sampling <ul style="list-style-type: none"> ■ Analyze all MW-series wells for selected inorganic parameters ■ Analyze selected MW-series wells for complete CLP organics and inorganics 	<ul style="list-style-type: none"> ■ Refine plume delineations ■ Assess plume/source area relationships ■ Evaluate possible impacts, if any, of unconfirmed source areas
<hr/>	
Seep Sampling <ul style="list-style-type: none"> ■ Base of construction scrap dump ■ Below plant recreation area ■ Steel conduit at eastern edge of Pond 5 	<ul style="list-style-type: none"> ■ Evaluate possible impacts, if any, of unconfirmed source areas
<hr/>	
Disposal Pond Characterization <ul style="list-style-type: none"> ■ Composite pond solids sample analyses ■ Pond perimeter soil borings ■ Double-ring infiltrometer testing 	<ul style="list-style-type: none"> ■ Provide additional data specifically requested by EPA and OEPA ■ Further characterize chemical make-up of pond solids ■ Assess vertical and lateral variations in pond solids composition ■ Evaluate physical characteristics of soils beneath ponds ■ Determine permeability of pond surfaces
<hr/>	

TASK BREAKDOWN**OBJECTIVES****Former Potliner Storage Area Characterization**

- Approximately 24 soil borings with continuous sampling
- 5 composite samples from each boring analyzed for indicator inorganics
- Selected samples analyzed for complete CLP organics and inorganics
- Characterize the presence in soils of residual potliner material
- Determine lateral and vertical extent of affected soils

Characterization of Ohio River Sediments

- Six samples to be analyzed for complete CLP organics and inorganics
- Assess possible facility-related alterations, if any, to Ohio River sediments

Assessment of Carbon Runoff and Deposition area

- Six samples of carbon deposits and six samples of underlying soils analyzed for CLP organics and inorganics
- Hand borings performed over 50-foot square grid
- Evaluate possible impacts, if any, of unconfirmed source area
- Determine lateral and vertical extent of deposition area

Plant Recreation Area Fill Investigation

- Soil borings with continuous sampling
- Visual inspection and logging of soil composition
- Determine if source material is present

Air Monitoring

- High-volume sampling for total respirable particulates
- Upwind and downwind samplers
- Provide additional data specifically requested by EPA and OEPA
- Attempt to quantify volume of respirable particulate if any, transported from suspected source areas by wind

TABLE 3.2-2

MATRIX OF DATA COLLECTION TASKS

Task	Sample/Data Type	Frequency	Objective
Additional Monitoring Wells	- Soil samples	Every five feet of penetration	Characterize soil type and qualitative physical properties
	- Ambient air monitoring	Continuously	Protection of field personnel
Ground-water sampling	- Well-head air monitoring	Prior to sampling each well	Protection of field personnel
	- Field analyses for temperature pH, and specific conductance	Following evacuation of each well	
	- Laboratory Analyses for selected inorganics	All MW-Series wells	Refine plume delineations Serve as baseline data for evaluating remedial system
	- Laboratory analysis for CLP parameters and other selected inorganics	Selected MW-series wells	Evaluate impacts, if any, of unconfirmed source areas
Disposal Pond Characterization	- Ambient air monitoring	Continuously	Protection of field personnel
	- Laboratory analysis of pond solids samples for CLP parameters and other selected inorganics	Composite samples from various depths and lateral locations in each pond	Determine chemical composition of pond solids and assess lateral and vertical variations
	- Double-ring infiltrometer-testing	Selected locations in each pond	Determine permeability of pond surfaces
Former Potliner Storage Area Characterization	- Ambient air monitoring	Continuously	Protection of field personnel
	- Soil samples	Composite sample every 2 feet in 24 borings	Characterize composition type and physical properties
	- Laboratory analyses for inorganic indicators	All composite samples	Assess vertical and horizontal extent of affected soils
	- Laboratory analyses for CLP parameters and other selected inorganics	All samples from 4 selected borings	Further characterization of soil composition
Characterization of Ohio River Sediments	- Laboratory analyses for CLP parameters and other selected inorganics	At six predetermined sampling locations	Assess possible facility-related alterations, if any, to river sediments

TABLE 3.2-2 (continued)
MATRIX OF DATA COLLECTION TASKS

Task	Sample/Data Type	Frequency	Objective
Carbon Runoff and Deposition area Assessment	<ul style="list-style-type: none"> - Soil samples - Laboratory analyses for CLP parameters and other selected inorganics 	<p>Continuously through carbon deposits over 50' x 50' grid</p> <p>On six samples of carbon material and six samples of underlying soil</p>	<p>Assess vertical and lateral extent of carbon deposition</p> <p>Determine chemical composition of carbon deposits</p> <p>Assess alterations, if any, to subsoil conditions</p>
Plant Recreation Area Fill Investigation	<ul style="list-style-type: none"> - Ambient air monitoring - Soil samples - Laboratory analyses of seep samples for CLP parameters and other selected inorganics 	<p>Continuously</p> <p>Continuously</p> <p>From 2 identified seeps</p>	<p>Protection of field personnel</p> <p>Evaluate composition of fill material</p> <p>Assess quality of fluids emanating from beneath fill</p>
Construction Material Scrap Dump Characterization	<ul style="list-style-type: none"> - Laboratory analyses of seep samples for CLP parameters and other selected inorganics 	<p>From 2 identified seeps</p>	<p>Assess quality of fluids emanating from beneath scrap dump material</p>
Air Monitoring	<ul style="list-style-type: none"> - High-volume samples of respirable particulates 	<p>24 hours, once every 6 days for 10 months from each sampling station</p>	<p>Attempt to quantify volume of respirable particulate transported from suspected source areas by wind</p>
Disposal Pond 5 Conduit Sampling	<ul style="list-style-type: none"> - Laboratory analyses for CLP parameters and other selected inorganics 	<p>From steel conduit on east berm</p>	<p>Assess quality of intermittent fluid discharges</p>

TABLE 3.2-3
SUMMARY OF PHASE I SAMPLING AND ANALYSIS PROGRAM

-1-

SAMPLE MATRIX	FIELD PARAMETERS	LABORATORY PARAMETERS	INVESTIGATIVE SAMPLES			REPLICATES			FIELD BLANKS			TRIP BLANKS			MATRIX TOTAL
			NO.	FREQ.	TOTAL	NO.	FREQ.	TOTAL	NO.	FREQ.	TOTAL	NO.	FREQ.	TOTAL	
Ground Water	pH	pH	52-55	1	52-55	5	1	5	9	1	9	---	---	---	66-69
		Specific Conductance	52-55	1	52-55	5	1	5	9	1	9	---	---	---	66-69
	Specific Conductance	Total Dissolved Solids	52-55	1	52-55	5	1	5	9	1	9	---	---	---	66-69
		Total Organic Carbon	52-55	1	52-55	5	1	5	9	1	9	---	---	---	66-69
		Alkalinity	52-55	1	52-55	5	1	5	9	1	9	---	---	---	66-69
	Temperature	Ammonia-N	52-55	1	52-55	5	1	5	9	1	9	---	---	---	66-69
		Chloride	52-55	1	52-55	5	1	5	9	1	9	---	---	---	66-69
	Health & Safety Air Monitoring *	Fluoride	52-55	1	52-55	5	1	5	9	1	9	---	---	---	66-69
		Sulfate	52-55	1	52-55	5	1	5	9	1	9	---	---	---	66-69
		Silica (dissolved)	52-55	1	52-55	5	1	5	9	1	9	---	---	---	66-69
		Cyanide (amenable)	52-55	1	52-55	5	1	5	9	1	9	---	---	---	66-69
		Cyanide (total)	52-55	1	52-55	5	1	5	9	1	9	---	---	---	66-69
		Tin	32-35	1	32-35	3	1	3	6	1	6	---	---	---	41-44
		CLP Metals	32-35	1	32-35	3	1	3	6	1	6	---	---	---	41-44
		Selected CLP Metals **	20	1	20	2	1	2	3	1	3	---	---	---	25
		Volatile Organic Parameters of the U.S. EPA CLP List	32-35	1	32-35	3	1	3	6	1	6	5	1	5	46-49
		Base Neutral/Acid Extractable Organic Compounds of the U.S. EPA CLP List	32-35	1	32-35	3	1	3	6	1	6	---	---	---	41-44
		Pesticides/PCBs of the U.S. EPA CLP List	32-35	1	32-35	3	1	3	6	1	6	---	---	---	41-44

QUALITY ASSURANCE PROGRAM
DEC 18 1987
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TABLE 3.2-3
SUMMARY OF PHASE I SAMPLING AND ANALYSIS PROGRAM

-2-

SAMPLE MATRIX	FIELD PARAMETERS	LABORATORY PARAMETERS	INVESTIGATIVE SAMPLES			REPLICATES			FIELD BLANKS			TRIP BLANKS			MATRIX TOTAL	
			NO.	FREQ.	TOTAL	NO.	FREQ.	TOTAL	NO.	FREQ.	TOTAL	NO.	FREQ.	TOTAL		
<hr/>																
Disposal Pond																
Solids	Health & Safety	pH	45	1	45	5	1	5	---	---	---	---	---	---	50	
	Air Monitoring *	Solids (% by weight)	45	1	45	5	1	5	---	---	---	---	---	---	50	
		Total Organic Carbon	45	1	45	5	1	5	---	---	---	---	---	---	50	
		Alkalinity	45	1	45	5	1	5	---	---	---	---	---	---	50	
		Ammonia-N	45	1	45	5	1	5	---	---	---	---	---	---	50	
		Chloride	45	1	45	5	1	5	---	---	---	---	---	---	50	
		Fluoride	45	1	45	5	1	5	---	---	---	---	---	---	50	
		Sulfate	45	1	45	5	1	5	---	---	---	---	---	---	50	
		Silica (SiO2)	45	1	45	5	1	5	---	---	---	---	---	---	50	
		Cyanide (amenable)	45	1	45	5	1	5	---	---	---	---	---	---	50	
		Cyanide (Total)	45	1	45	5	1	5	---	---	---	---	---	---	50	
	Inorganic Parameters of the U.S. EPA CLP List		45	1	45	5	1	5	---	---	---	---	---	---	50	
	Volatile Organic Parameters of the U.S. EPA CLP List		45	1	45	5	1	5	---	---	---	---	---	---	50	
	Base Neutral/Acid Extractable Compounds of the U.S. EPA CLP List		45	1	45	5	1	5	---	---	---	---	---	---	50	
	PCBs		45	1	45	5	1	5	---	---	---	---	---	---	50	
	Former Potliner															
	Storage Area Soils	Health & Safety	pH	120	1	120	12	1	12	---	---	---	---	---	---	132
		Air Monitoring *	Ammonia-N	120	1	120	12	1	12	---	---	---	---	---	---	132
			Calcium	120	1	120	12	1	12	---	---	---	---	---	---	132
Sodium			120	1	120	12	1	12	---	---	---	---	---	---	132	
Fluoride			120	1	120	12	1	12	---	---	---	---	---	---	132	
Cyanide (total)			120	1	120	12	1	12	---	---	---	---	---	---	132	
Inorganic Parameters of the U.S. EPA CLP List		20-40	1	20-40	2-4	1	2-4	---	---	---	---	---	---	22-44		
Volatile Organic Parameters the U.S. EPA CLP List		20-40	1	20-40	2-4	1	2-4	---	---	---	---	---	---	22-44		
Base Neutral/Acid Extractable Compounds of the U.S. EPA CLP List		20-40	1	20-40	2-4	1	2-4	---	---	---	---	---	---	22-44		
PCBs		20-40	1	20-40	2-4	1	2-4	---	---	---	---	---	---	22-44		

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PROTECTION
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RECORDS
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PROTECTION
AGENCY
RECORDS
DATE 11/19/91

TABLE 3.2-3
SUMMARY OF PHASE I SAMPLING AND ANALYSIS PROGRAM
(continued)

-3-

SAMPLE MATRIX	FIELD PARAMETERS	LABORATORY PARAMETERS	INVESTIGATIVE SAMPLES			REPLICATES			FIELD BLANKS			TRIP BLANKS			MATRIX TOTAL
			NO.	FREQ.	TOTAL	NO.	FREQ.	TOTAL	NO.	FREQ.	TOTAL	NO.	FREQ.	TOTAL	
River Sediments	Not Applicable	pH	6	1	6	1	1	1	---	---	---	---	---	---	7
		Total Organic Carbon	6	1	6	1	1	1	---	---	---	---	---	---	7
		Alkalinity	6	1	6	1	1	1	---	---	---	---	---	---	7
		Ammonia-N	6	1	6	1	1	1	---	---	---	---	---	---	7
		Silica (dissolved)	6	1	6	1	1	1	---	---	---	---	---	---	7
		Chloride	6	1	6	1	1	1	---	---	---	---	---	---	7
		Fluoride	6	1	6	1	1	1	---	---	---	---	---	---	7
		Sulfate	6	1	6	1	1	1	---	---	---	---	---	---	7
		Cyanide (amenable)	6	1	6	1	1	1	---	---	---	---	---	---	7
		Cyanide (total)	6	1	6	1	1	1	---	---	---	---	---	---	7
		Inorganic Parameters of the U.S. EPA CLP List	6	1	6	1	1	1	---	---	---	---	---	---	7
		Volatile Organic Parameters of the U.S. EPA CLP List	6	1	6	1	1	1	---	---	---	---	---	---	7
		Base Neutral/Acid Extractable Compounds of the U.S. EPA CLP List	6	1	6	1	1	1	---	---	---	---	---	---	7
		PCB (if found in disposal pond solids or former potliner area soils)	6	1	6	1	1	1	---	---	---	---	---	---	7
Carbon Deposition Area Carbon Material	Health & Safety Air Monitoring *	pH	6	1	6	1	1	1	---	---	---	---	---	---	7
		Total Organic Carbon	6	1	6	1	1	1	---	---	---	---	---	---	7
		Alkalinity	6	1	6	1	1	1	---	---	---	---	---	---	7
		Silica (SiO2)	6	1	6	1	1	1	---	---	---	---	---	---	7
		Chloride	6	1	6	1	1	1	---	---	---	---	---	---	7
		Fluoride	6	1	6	1	1	1	---	---	---	---	---	---	7
		Sulfate	6	1	6	1	1	1	---	---	---	---	---	---	7
		Cyanide (amenable)	6	1	6	1	1	1	---	---	---	---	---	---	7
		Cyanide (total)	6	1	6	1	1	1	---	---	---	---	---	---	7
		Inorganic Parameters of the U.S. EPA CLP List	6	1	6	1	1	1	---	---	---	---	---	---	7
		Volatile Organic Parameters of the U.S. EPA CLP List	6	1	6	1	1	1	---	---	---	---	---	---	7
		Base Neutral/Acid Extractable Compounds of the U.S. EPA CLP List	6	1	6	1	1	1	---	---	---	---	---	---	7

QUALITY ASSURANCE PROGRAM
 DEC 18 1987
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TABLE 3.2-3
SUMMARY OF PHASE I SAMPLING AND ANALYSIS PROGRAM
(continued)

-4-

SAMPLE MATRIX	FIELD PARAMETERS	LABORATORY PARAMETERS	INVESTIGATIVE SAMPLES			REPLICATES			FIELD BLANKS			TRIP BLANKS			MATRIX TOTAL
			NO.	FREQ.	TOTAL	NO.	FREQ.	TOTAL	NO.	FREQ.	TOTAL	NO.	FREQ.	TOTAL	
Carbon Deposition Area Soils	Health & Safety Air Monitoring *	pH	6	1	6	1	1	1	---	---	---	---	---	---	7
		Total Organic Carbon	6	1	6	1	1	1	---	---	---	---	---	---	7
		Alkalinity	6	1	6	1	1	1	---	---	---	---	---	---	7
		Silica (SiO2)	6	1	6	1	1	1	---	---	---	---	---	---	7
		Chloride	6	1	6	1	1	1	---	---	---	---	---	---	7
		Fluoride	6	1	6	1	1	1	---	---	---	---	---	---	7
		Sulfate	6	1	6	1	1	1	---	---	---	---	---	---	7
		Cyanide (amenable)	6	1	6	1	1	1	---	---	---	---	---	---	7
		Cyanide (Total)	6	1	6	1	1	1	---	---	---	---	---	---	7
		Inorganic Parameters of the U.S. EPA CLP List	6	1	6	1	1	1	---	---	---	---	---	---	7
		Volatile Organic Parameters of the U.S. EPA CLP List	6	1	6	1	1	1	---	---	---	---	---	---	7
		Base Neutral/Acid Extractable Compounds of the U.S. EPA CLP List	6	1	6	1	1	1	---	---	---	---	---	---	7
Ground Water Seeps and Pond 5 Conduit	Health & Safety Air Monitoring *	pH	5	1	5	1	1	1	1	1	1	---	---	---	7
		Specific Conductance	5	1	5	1	1	1	1	1	1	---	---	---	7
		Total Dissolved Solids	5	1	5	1	1	1	1	1	1	---	---	---	7
		Total Organic Carbon	5	1	5	1	1	1	1	1	1	---	---	---	7
		Alkalinity	5	1	5	1	1	1	1	1	1	---	---	---	7
		Silica (dissolved)	5	1	5	1	1	1	1	1	1	---	---	---	7
		Chloride	5	1	5	1	1	1	1	1	1	---	---	---	7
		Fluoride	5	1	5	1	1	1	1	1	1	---	---	---	7
		Sulfate	5	1	5	1	1	1	1	1	1	---	---	---	7
		Ammonia-N	5	1	5	1	1	1	1	1	1	---	---	---	7
		Cyanide (amenable)	5	1	5	1	1	1	1	1	1	---	---	---	7
		Cyanide (total)	5	1	5	1	1	1	1	1	1	---	---	---	7
		Inorganic Parameters of the U.S. EPA CLP List	5	1	5	1	1	1	1	1	1	---	---	---	7
		Volatile Organic Parameters of the U.S. EPA CLP List	5	1	5	1	1	1	1	1	1	1	1	1	8
		Base Neutral/Acid Extractable Compounds of the U.S. EPA CLP List	5	1	5	1	1	1	1	1	1	---	---	---	7
Air Monitoring Respirable Dust	Not Applicable	Respirable Dust	200	1	200	---	---	---	---	---	---	---	---	---	200
		- wt. per unit vol. air													

PROJECT NUMBER 800-258-1000-1

DEC 18 1987

QUALITY ASSURANCE DIVISION

2

1

TABLE 3.2-3
SUMMARY OF PHASE I SAMPLING AND ANALYSIS PROGRAM
(continued)

Notes: Only those aqueous samples designated for analysis of metals shall be field filtered prior to preservation. Filtration shall be through a glass fiber prefilter.

For aqueous samples, twice the normal sample volume is necessary to perform matrix spike/matrix spike duplicate analyses for volatile organic compounds and three times the normal sample volume is necessary to perform matrix spike/matrix spike duplicate analyses for extractables and pesticides/PCB (where appropriate). Kemron shall provide sample containers that permit collection of adequate sample volumes so that these analyses may be performed.

- * Health and safety air monitoring shall be performed for the protection of the field personnel. Data generated by the health and safety air monitoring shall not be used in the evaluation of site conditions for purposes of selecting remedial alternatives.

** List of selected CLP Metals includes:

Aluminum	Cobalt	Nickel
Arsenic	Copper	Potassium
Barium	Iron (total)	Selenium
Cadmium	Lead	Sodium
Calcium	Magnesium	Zinc
Chromium (total)	Manganese	

DEC 18 1987
FEDERAL BUREAU OF INVESTIGATION
U.S. DEPARTMENT OF JUSTICE

TABLE 3.2-4

DETECTION LIMITS FOR PARAMETERS
TO BE ANALYZED FOR DURING
PHASE I RI

Q. 177 ADDITIONAL PHASE

DEC 18 1987

ENVIRONMENTAL SERVICES DIVISION

Target Compound List (TCL) and
Contract Required Quantitation Limits (CRQL)*

Volatiles	CAS Number	Quantitation Limits**	
		Water ug/L	Low Soil/Sediment ^a ug/Kg
1. Chloromethane	74-87-3	10	10
2. Bromomethane	74-83-9	10	10
3. Vinyl Chloride	75-01-4	10	10
4. Chloroethane	75-00-3	10	10
5. Methylene Chloride	75-09-2	5	5
6. Acetone	67-64-1	10	10
7. Carbon Disulfide	75-15-0	5	5
8. 1,1-Dichloroethene	75-35-4	5	5
9. 1,1-Dichloroethane	75-34-3	5	5
10. 1,2-Dichloroethene (total)	540-59-0	5	5
11. Chloroform	67-66-3	5	5
12. 1,2-Dichloroethane	107-06-2	5	5
13. 2-Butanone	78-93-3	10	10
14. 1,1,1-Trichloroethane	71-55-6	5	5
15. Carbon Tetrachloride	56-23-5	5	5
16. Vinyl Acetate	108-05-4	10	10
17. Bromodichloromethane	75-27-4	5	5
18. 1,2-Dichloropropane	78-87-5	5	5
19. cis-1,3-Dichloropropene	10061-01-5	5	5
20. Trichloroethene	79-01-6	5	5
21. Dibromochloromethane	124-48-1	5	5
22. 1,1,2-Trichloroethane	79-00-5	5	5
23. Benzene	71-43-2	5	5
24. trans-1,3-Dichloropropene	10061-02-6	5	5
25. Bromoform	75-25-2	5	5
26. 4-Methyl-2-pentanone	108-10-1	10	10
27. 2-Hexanone	591-78-6	10	10
28. Tetrachloroethene	127-18-4	5	5
29. Toluene	108-88-3	5	5
30. 1,1,2,2-Tetrachloroethane	79-34-5	5	5

(continued)

TABLE 3.2-4
(continued)

CLINTON COUNTY, OHIO

DEC 18 1987

ENVIRONMENTAL SERVICES

Semivolatiles	CAS Number	Quantitation Limits**	
		Water ug/L	Low Soil/Sediment ^b ug/Kg
65. Dimethylphthalate	131-11-3	10	330
66. Acenaphthylene	208-96-8	10	330
67. 2,6-Dinitrotoluene	606-20-2	10	330
68. 3-Nitroaniline	99-09-2	50	1600
69. Acenaphthene	83-32-9	10	330
70. 2,4-Dinitrophenol	51-28-5	50	1600
71. 4-Nitrophenol	100-02-7	50	1600
72. Dibenzofuran	132-64-9	10	330
73. 2,4-Dinitrotoluene	121-14-2	10	330
74. Diethylphthalate	84-66-2	10	330
75. 4-Chlorophenyl-phenyl ether	7005-72-3	10	330
76. Fluorene	86-73-7	10	330
77. 4-Nitroaniline	100-01-6	50	1600
78. 4,6-Dinitro-2-methylphenol	534-52-1	50	1600
79. N-nitrosodiphenylamine	86-30-6	10	330
80. 4-Bromophenyl-phenylether	101-55-3	10	330
81. Hexachlorobenzene	118-74-1	10	330
82. Pentachlorophenol	87-86-5	50	1600
83. Phenanthrene	85-01-8	10	330
84. Anthracene	120-12-7	10	330
85. Di-n-butylphthalate	84-74-2	10	330
86. Fluoranthene	206-44-0	10	330
87. Pyrene	129-00-0	10	330
88. Butylbenzylphthalate	85-68-7	10	330
89. 3,3'-Dichlorobenzidine	91-94-1	20	660
90. Benzo(a)anthracene	56-55-3	10	330
91. Chrysene	218-01-9	10	330
92. bis(2-Ethylhexyl)phthalate	117-81-7	10	330
93. Di-n-octylphthalate	117-84-0	10	330
94. Benzo(b)fluoranthene	205-99-2	10	330

(continued)

TABLE 3.2-4
(continued)

QUALITY ASSURANCE PROGRAM

DEC 18 1987

ENVIRONMENT SERVICES DIVISION

Semivolatiles	CAS Number	Quantitation Limits**	
		Water ug/L	Low Soil/Sediment ^b ug/Kg
95. Benzo(k)fluoranthene	207-08-9	10	330
96. Benzo(a)pyrene	50-32-8	10	330
97. Indeno(1,2,3-cd)pyrene	193-39-5	10	330
98. Dibenzo(a,h)anthracene	53-70-3	10	330
99. Benzo(g,h,i)perylene	191-24-2	10	330

^bMedium Soil/Sediment Contract Required Quantitation Limits (CRQL) for Semi-Volatile TCL Compounds are 60 times the individual Low Soil/Sediment CRQL.

*Specific quantitation limits are highly matrix dependent. The quantitation limits listed herein are provided for guidance and may not always be achievable.

**Quantitation limits listed for soil/sediment are based on wet weight. The quantitation limits calculated by the laboratory for soil/sediment, calculated on dry weight basis as required by the contract, will be higher.

TABLE 3.2-4
(continued)

ENVIRONMENTAL

DEC 18 1987

ENVIRONMENT SERVICES

Target Compound List (TCL) and
Contract Required Quantitation Limits (CRQL)*

Pesticides/PCBs	CAS Number	Quantitation Limits**	
		Water ug/L	Low Soil/Sediment ^c ug/Kg
100. alpha-BHC	319-84-6	0.05	8.0
101. beta-BHC	319-85-7	0.05	8.0
102. delta-BHC	319-86-8	0.05	8.0
103. gamma-BHC (Lindane)	58-89-9	0.05	8.0
104. Heptachlor	76-44-8	0.05	8.0
105. Aldrin	309-00-2	0.05	8.0
106. Heptachlor epoxide	1024-57-3	0.05	8.0
107. Endosulfan I	959-98-8	0.05	8.0
108. Dieldrin	60-57-1	0.10	16.0
109. 4,4'-DDE	72-55-9	0.10	16.0
110. Endrin	72-20-8	0.10	16.0
111. Endosulfan II	33213-65-9	0.10	16.0
112. 4,4'-DDD	72-54-8	0.10	16.0
113. Endosulfan sulfate	1031-07-8	0.10	16.0
114. 4,4'-DDT	50-29-3	0.10	16.0
115. Methoxychlor	72-43-5	0.5	80.0
116. Endrin ketone	53494-70-5	0.10	16.0
117. alpha-Chlordane	5103-71-9	0.5	80.0
118. gamma-Chlordane	5103-74-2	0.5	80.0
119. Toxaphene	8001-35-2	1.0	160.0
120. Aroclor-1016	12674-11-2	0.5	80.0
121. Aroclor-1221	11104-28-2	0.5	80.0
122. Aroclor-1232	11141-16-5	0.5	80.0
123. Aroclor-1242	53469-21-9	0.5	80.0
124. Aroclor-1248	12672-29-6	0.5	80.0
125. Aroclor-1254	11097-69-1	1.0	160.0
126. Aroclor-1260	11096-82-5	1.0	160.0

^cMedium Soil/Sediment Contract Required Quantitation Limits (CRQL) for Pesticide/PCB TCL compounds are 15 times the individual Low Soil/Sediment CRQL.

*Specific quantitation limits are highly matrix dependent. The quantitation limits listed herein are provided for guidance and may not always be achievable.

**Quantitation limits listed for soil/sediment are based on wet weight. The quantitation Limits calculated by the laboratory for soil/sediment, calculated on dry weight basis as required by the contract, will be higher.

DEC 18 1987

TABLE 3.2-4
(continued)

ENVIRONMENT SERVICES DIVISION

Target Compound List (TCL) and
Contract Required Quantitation Limits (CRQL)*

Semivolatiles	CAS Number	Quantitation Limits**	
		Water ug/L	Low Soil/Sediment ^b ug/Kg
35. Phenol	108-95-2	10	330
36. bis(2-Chloroethyl) ether	111-44-4	10	330
37. 2-Chlorophenol	95-57-8	10	330
38. 1,3-Dichlorobenzene	541-73-1	10	330
39. 1,4-Dichlorobenzene	106-46-7	10	330
40. Benzyl alcohol	100-51-6	10	330
41. 1,2-Dichlorobenzene	95-50-1	10	330
42. 2-Methylphenol	95-48-7	10	330
43. bis(2-Chloroisopropyl) ether	108-60-1	10	330
44. 4-Methylphenol	106-44-5	10	330
45. N-Nitroso-di-n- dipropylamine	621-64-7	10	330
46. Hexachloroethane	67-72-1	10	330
47. Nitrobenzene	98-95-3	10	330
48. Isophorone	78-59-1	10	330
49. 2-Nitrophenol	88-75-5	10	330
50. 2,4-Dimethylphenol	105-67-9	10	330
51. Benzoic acid	65-85-0	50	1600
52. bis(2-Chloroethoxy) methane	111-91-1	10	330
53. 2,4-Dichlorophenol	120-83-2	10	330
54. 1,2,4-Trichlorobenzene	120-82-1	10	330
55. Naphthalene	91-20-3	10	330
56. 4-Chloroaniline	106-47-8	10	330
57. Hexachlorobutadiene	87-68-3	10	330
58. 4-Chloro-3-methylphenol (para-chloro-meta-cresol)	59-50-7	10	330
59. 2-Methylnaphthalene	91-57-6	10	330
60. Hexachlorocyclopentadiene	77-47-4	10	330
61. 2,4,6-Trichlorophenol	88-06-2	10	330
62. 2,4,5-Trichlorophenol	95-95-4	50	1600
63. 2-Chloronaphthalene	91-58-7	10	330
64. 2-Nitroaniline	88-74-4	50	1600

(continued)

TABLE 3.2-4
(continued)

QUALITY ASSURANCE PROGRAM

DEC 18 1987

ENVIRONMENT SERVICES DIVISION

Volatiles	CAS Number	Quantitation Limits**	
		Water ug/L	Low Soil/Sediment ^a ug/Kg
31. Chlorobenzene	108-90-7	5	5
32. Ethyl Benzene	100-41-4	5	5
33. Styrene	100-42-5	5	5
34. Xylenes (Total)	1330-20-7	5	5

*Medium Soil/Sediment Contract Required Quantitation Limits (CRQL) for Volatile TCL Compounds are 125 times the individual Low Soil/Sediment CRQL.

*Specific quantitation limits are highly matrix dependent. The quantitation limits listed herein are provided for guidance and may not always be achievable.

**Quantitation limits listed for soil/sediment are based on wet weight. The quantitation limits calculated by the laboratory for soil/sediment, calculated on dry weight basis as required by the contract, will be higher.

TABLE 3.2-4
(continued)

QUALITY ASSURANCE REPORT

DEC 18 1997

ENVIRONMENTAL SCIENCE

Elements Determined by Inductively Coupled
Plasma Emission or Atomic Absorption Spectroscopy

Element	Contract Required Detection Level (1,2) (ug/L)
Aluminum	200
Antimony	60
Arsenic	10
Barium	200
Beryllium	5
Cadmium	5
Calcium	5000
Chromium	10
Cobalt	50
Copper	25
Iron	100
Lead	5
Magnesium	5000
Manganese	15
Mercury	0.2
Nickel	40
Potassium	5000
Selenium	5
Silver	10
Sodium	5000
Thallium	10
Vanadium	50
Zinc	20
Cyanide	10

NOTE: These CRDL are the instrument detection limits obtained in pure water. The actual detection limits for samples may be considerably higher depending on the sample matrix.

DEC 18 1987

TABLE 3.2-4
(continued)

ENVIRONMENTAL SERVICES

DETECTION LIMITS FOR NON-CLP INORGANIC PARAMETERS

	WATER <u>mg/l</u>	SOIL/SLUDGE <u>mg/kg</u>
Alkalinity	1	10
Ammonia, Nitrogen	0.1	1
Calcium	0.01	0.1
Chloride	1	10
Cyanide, Total	0.01	0.1
Dissolved Solids, Total	10	10
Fluoride	0.1	1
Organics Carbon, Total	1	10
Silica	2	20
Sodium	0.002	0.02
Solids, Total	10	10
Sulfate	1	10
Tin	0.005	0.05

These estimated detection limits can fluctuate based upon matrix interferences and sample volume used.

3.3 PROJECT ORGANIZATION AND RESPONSIBILITY

3.3.1 Project Personnel

Ormet has the overall responsibility for the initiation and direction of this RI, and has contracted Geraghty & Miller, Inc. to direct and supervise the tasks required by the Statement of Work. Qualifications of key G&M personnel are provided in Appendix E.

The principal parties involved in the performance of the RI are shown in the organizational chart in Figure 3.3-1. The addresses and phone numbers for the project supervisory personnel are listed below.

U.S. EPA Region V
Waste Management Division
230 Dearborn Street
Chicago, Illinois 60604
Phone: (312) 886-7278
Pauline M. LeBlanc
- U.S. EPA Project Coordinator

Ohio EPA
Southeast District Office
2195 Front Street
Logan, Ohio 43138
Phone: (614) 385-8501
Ken Dewey
- OEPA Project Coordinator

Ormet Corporation
P.O. Box 176
Hannibal, Ohio 43931
Phone: (614) 483-1381
T. A. Hermeling, Telephone Ext. 561
- Ormet Project Coordinator
John Reggi, Telephone Ext. 587
- Ormet Project Liason

Geraghty & Miller, Inc.
429 Washington Trust Building
Washington, Pennsylvania 15301
Phone: (412) 225-8615
Cleason P. Smith
- G&M Project Director
Robert L. Fargo
- G&M Project Manager
Timothy T. Ratvasky
- G&M QA/QC Officer/Site
Safety Officer

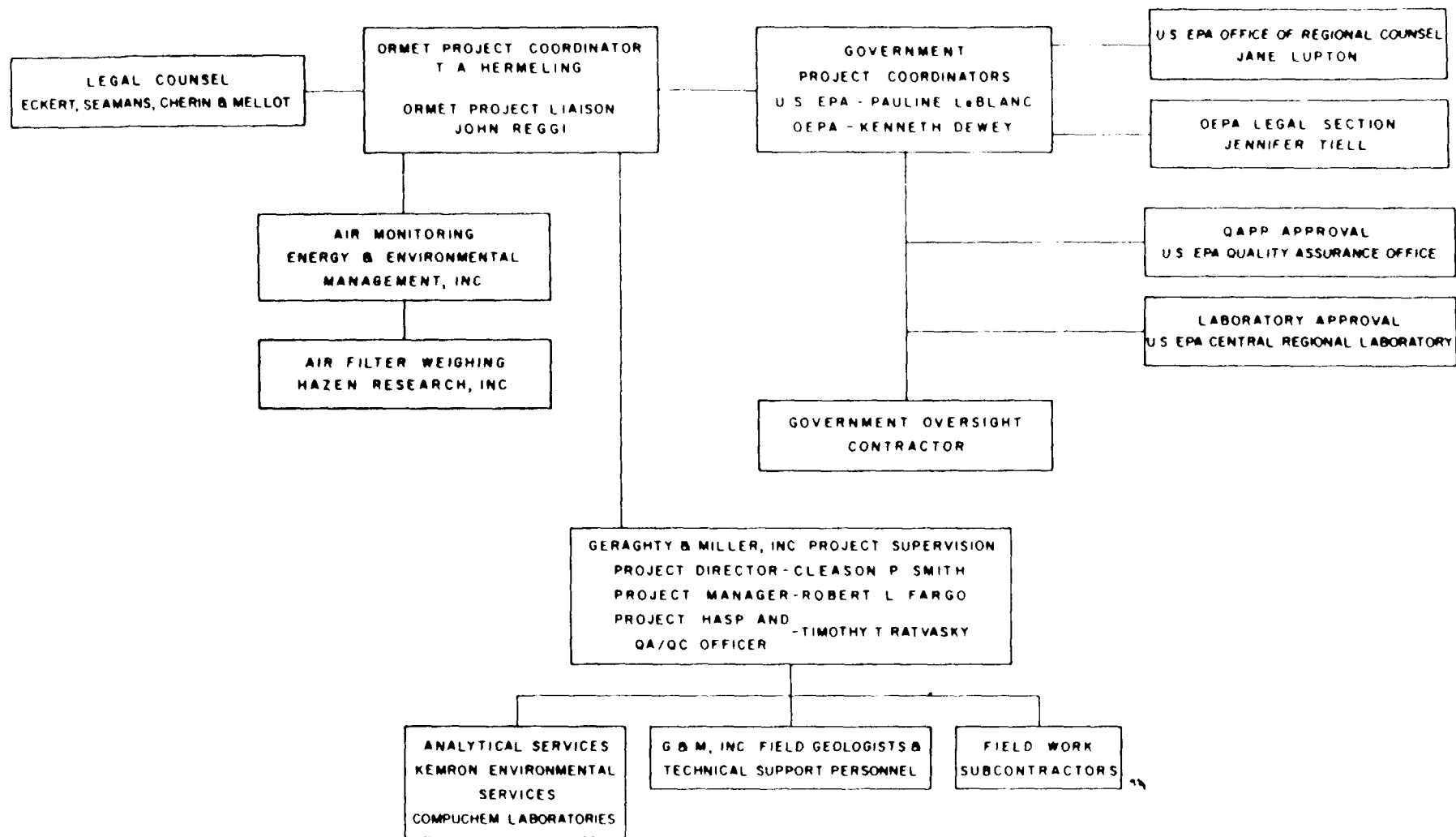


FIGURE 3.3-1. General Organizational Chart for Performance of Phase I RI.

DEC 18 1987

Section No. 3.3
Revision No. 3
Date: 12-11-87
Page 2 of 4

ENVIRONMENT SERVICES DIVISION

All data generated during the Phase I RI will be reviewed and assessed by the G&M Project Manager and the G&M QA/QC Officer, with final review by the G&M Project Director. Responsibility for all quality assurance/quality control review is with the G&M QA/QC Officer. If quality assurance problems or deficiencies are encountered, the appropriate corrective modifications will be identified with the input of the G&M QA/QC Officer.

Laboratory analytical testing of field samples for organic and non-CLP List inorganic parameters will be performed by Kemron. The QA/QC Coordinator and Project Director for Kemron will be David Bumgarner. The Laboratory Manager is Jean Anderson, with Wayne Wang as the Supervisor of Organics Analyses and Beverly Cornwell as the Supervisor of Inorganics Analyses. Analyses of field samples for the inorganic parameters of the U.S. EPA CLP List will be conducted by CompuChem Laboratories, Inc., a participant of the Contract Laboratory Program. Internal quality assurance procedures to be followed by Kemron and CompuChem are outlined in Section 3.9. The weighing of the air monitor filters will be performed by Hazen Research, Inc.

External performance and system audits of the laboratories supplying analytical services for the Phase I RI shall be conducted by the U.S. EPA Region V Central Regional Laboratory.

3.4 QUALITY ASSURANCE OBJECTIVES

The primary quality assurance objective is to make certain that the data generated during the RI is of known and acceptable quality. Data collection efforts will adhere to QA/QC procedures developed by G&M for the collection, preservation, and custody of field samples. Procedures specific to each task of the RI including the collection of quality-control samples (e.g., field blanks, replicates, trip blanks, etc.) are provided in Section 3.10.

The goal for the precision and accuracy assessment process is to produce data of a quality which meets or exceeds the minimum industry (method) standards. The data so generated shall be sufficiently documented to be legally defensible. The goals for accuracy, precision, and completeness are given in more detail in the specific EPA methods of the CLP protocol.

The procedures used to assess the accuracy and precision of the organic analyses include:

- 1) Maintaining records of surrogate spike recovery
- 2) Analysis of laboratory reagent blanks
- 3) Analysis of matrix spikes and matrix spike duplicates
- 4) Monitoring of areas of internal standards
- 5) Initial five point calibration curves
- 6) Continuing calibration compounds (CCC) standards every 12 hours

The procedures to be used in assessing the accuracy and precision of the inorganic analyses include:

- 1) Analysis of a method blank
- 2) Analysis of a reference standard
- 3) Duplicate sample analysis
- 4) Matrix spike analysis

Further details pertaining to the assessment of accuracy, precision, and completeness are provided in Section 3.9.

Specific QA/QC procedures to be followed by Kemron and CompuChem in performing chemical analyses, including quality assurance objectives, are described in Section 3.9. The level of effort for quality-control samples adopted by the laboratories, plus the analytical method, sensitivity, accuracy, and precision, are also provided in Section 3.9.

3.4.1 Precision

The QA/QC aim in testing for precision is to demonstrate the reproducibility of the data. The precision of measurements made during the project will: (a) be evaluated and reported along with the method reference; (b) use high purity materials, standards, solutions, knowledgeable personnel, procedures consistent with scientific practice, and internal quality controls; and (c) be consistent.

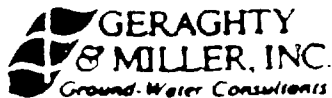
3.6.1 Drilling and Monitor-Well Installation

3.6.1.1 Soil Boring Procedures

The soil boring procedures described in this section apply to the borings to be performed during the characterization of the former potliner storage area (Section 2.2), the investigation of the plant recreation area fill materials (Section 2.9), and the installation of the disposal pond perimeter borings (Section 2.1). On a daily basis, the G&M Field Geologist shall maintain a drilling checklist as shown in Figure 3.6-1.

Soil borings to be performed at the Ormet facility shall be advanced via hollow stem auger (HSA) drilling. Soil samples will be collected continuously using a 2-foot-long split-spoon sampling device in accordance with ASTM Method D1586-84, "Standard Method for Penetration Test and Split-Barrel Sampling of Soils," which is provided as Reference 2 at the end of this QAPP.

Upon retrieving each split-spoon sample, the soil core will be removed and inspected and described for gross composition, texture, and other observable properties following standardized G&M procedures. A detailed description of these procedures is given as Reference 3 at the end of this QAPP. The standard form to be used in logging soil sample descriptions is provided in Figure 3.6-2.



DRILLING & INSTALLATION OF MONITORING WELLS DAILY CHECKLIST

PROJECT: _____

WELLS/BORINGS: _____

LOCATION: _____

DATE: _____

G&M PERSONNEL ON SITE: _____

TIME: _____

CHECKED BY: _____

ITEMS	OK/NA	COMMENTS
PRIOR TO DRILLING:		
Site checked for underground utilities		
Well locations staked		
Well drilling permits secured		
G&M QA Manual/QA plan available		
Health & Safety plan (HASP) available		
Safety equipment on site		
Contractor equipment adequate		
Drilling equipment steam cleaned		
Drilling water source approved/sampled		
Drilling equipment water sample taken		
Drilling mud & additives approved		
Sand or gravel pack sample approved		
ut composition approved		
DURING INSTALLATION:		
Formation samples properly taken and		
bottled or bagged		
Rock color chart used		
OVA monitoring during drilling & sampling		
Cores properly marked and stored		
Hard hat worn		
Proper safety procedures followed		
Hazardous soil, mud or water properly disposed		
Daily Log kept		
Sample/Core Log form filled out		
Well Construction Log prepared		
Materials/Cost Log prepared		
Location Sketch made		
Tremie pipe used in grouting		
Abandoned well/boring grouted & staked		
Protective casing/well cap/lock installed		
Well identification no. attached		
Well development adequate		
Well elevation and location surveyed in		
Additional Comments:		

FIGURE 3.6-1 Daily checklist for drilling and monitor-well installation activities

SAMPLE/CORE LOG

Boring/Well _____ Project/No. _____ Page _____ of _____

Site Location _____	Drilling Started _____	Drilling Completed _____
---------------------	------------------------	--------------------------

Total Depth Drilled _____ feet Hole Diameter _____ inches Type of Sample/
Coring Device _____

Length and Diameter of Coring Device _____ Sampling Interval _____ feet

Land-Surface Elev. _____ feet ☐ Surveyed ☐ Estimated Datum _____

Drilling Fluid Used _____ Drilling Method _____

Drilling Contractor _____ Driller _____ Helper _____

Prepared _____ Hammer _____ Hammer _____
By _____ Weight _____ Drop _____ inches

[illegible]

In routine sampling programs, a soil composite from each sample will be placed in a glass jar (1/2 pint) with a water-tight lid and labeled to indicate sample location, date of collection, depth interval, blow counts, and the name of the field geologist. This information will also be written on the lid of the sample jar with a waterproof marking pen. Figure 3.6-3 shows the label which will be affixed to each sample jar.

During the characterization of the former potliner storage area, where soil samples will be subjected to laboratory analyses, special sample collection and packaging techniques will be applied. Upon retrieval of the sample from each two-foot interval, the sample will be described as discussed above. Then, the contents of the split-spoon will be placed in a glass container and gently mixed to form a composite. Each of the 120 composites (5 composites from each of 24 borings) shall be split to provide two samples for each interval.

The initial 120 soil samples which are to be analyzed for six inorganic indicator parameters (i.e., calcium, sodium, fluoride, ammonia-nitrogen, pH and total cyanide) will be placed in the appropriate sample containers (see Table 3.6-3) and cooled to approximately 4°C for shipment to the laboratory. Transport of the soil samples will be monitored via chain-of

GERAGHTY & MILLER, INC.

Project # _____
Client Name _____
Boring # _____
Sample # _____
Depth _____
Blows / / /
Recovery _____
Date _____

FIGURE 3.6-3 Standard label to be completed and affixed to soil sample jars.

custody procedures outlined in Section 3.7. The 120 split samples, which are to be held until the results of the original inorganics analyses are received so that 20 samples can be selected for complete CLP List analysis, shall be placed in appropriate containers supplied by the laboratory. These samples shall be properly stored at the selected laboratory. Replicate soil samples shall be prepared and submitted for analysis at a rate of 10 percent. Therefore, 12 replicates will be submitted for analysis of the inorganic indicator parameters and 2 replicates will be submitted for analysis for CLP List parameters.

After each sampling interval, the split-spoon device will undergo a multi-step washdown to reduce the risk of cross-contaminating samples. First, the split spoon will be brushed with a dry brush to remove the bulk of any remaining soil. This residual soil from the split spoon will be distributed on the ground in the immediate vicinity of the boring from which the sample is collected. The spoon will then be washed in a solution of Sparkleen soap, followed by a rinse in clean tap water, then a distilled water rinse. The Sparkleen soap wash water and the rinse water, which will be collected in a bucket beneath each rinse spigot, shall be placed in the same container used to collect the drilling rig washdown water after each boring.

Following completion of each soil boring, the borehole shall be backfilled with thick bentonite slurry to within approximately two (2) feet of land surface. The slurry will be mixed as thick as can be circulated through the mixing pump. This produces a slurry that is generally thick enough to reduce migration into the unsaturated zone. A tremmie pipe will be used to install the slurry, allowing the borehole to be backfilled from the bottom up. This reduces the potential for creating void spaces in the column of bentonite. The remaining upper 2 feet will be filled up to ground surface with neat cement. The boring location will be marked with a wooden stake inserted into the cement. The stake will be marked to indicate the boring number, total depth, and date.

Each boring will be surveyed by a licensed surveyor to determine its map coordinates to within ± 3 feet. Elevations of the ground surface (i.e., the top of the cement surface plug) at each boring will be surveyed to within ± 0.10 -foot accuracy to facilitate stratigraphic correlation and cross-section preparation.

The decontamination process will require that the rig be driven into the washdown trench and all equipment to be cleaned will be unloaded onto the plastic. A steam cleaner, utilizing a Sparkleen soap solution will be used to wash down the equipment and also the rear of the drilling rig (before leaving the site at the end of the field program, the entire rig will be washed). Sparkleen was chosen because it does not contain ammonia (one of the indicator parameters at the site) and is low in phosphates, but still possesses a surfactant for removing oils and greases. The steam cleaner will then be switched to a clean water source and the equipment and the rig shall be rinsed. The runoff water from the washdown operation will be carried from the trench, through the diversion ditch to the sump, where it will be pumped to a large holding tank. After the field program has concluded, the water in the holding tank will be sampled and analyzed for the inorganic and organic parameters of the U.S. EPA CLP List (excluding PCBs, pesticides, and dioxin) and other selected plant-related indicator parameters. Pending the results of these analyses, ~~alternatives for the disposal of the washdown water will be developed.~~

3.6.2 Disposal Pond Sampling Procedures

During Phase I of the RI, solids samples shall be collected from each of the five disposal ponds at the site. Samples will

be collected at a number of horizontal locations in each pond and composited for a variety of predetermined depth intervals according to the sampling scheme detailed in Section 2.1.

Previous disposal pond sampling activities (see Section 1.2.2) have indicated that the upper 2 to 4 feet of material in the ponds is relatively dry and capable of supporting at least moderate weight. Below 2 to 4 feet the consistency of the pond material changes to a saturated oozy sludge.

At each sampling location, the uppermost sample (i.e., at the pond surface) will be collected using a hand-augering device equipped with a three-inch-diameter stainless steel collection barrel. Samples from the deeper sampling intervals shall be collected utilizing a liquid sludge sampling device developed by Geraghty & Miller, Inc. (see Figure 3.6-6). This instrument consists of 5-foot-long sections of 2-inch diameter, threaded flush-joint PVC pipe. To control the intake of sample, a bottom plug is connected to a small-diameter steel rod, which runs through the center of the PVC pipe. By pushing on the steel rod, the bottom plug can be separated from the end of the pipe, opening the device for sample intake, and then pulled back into place. To facilitate sampling at depths greater than five feet, additional five foot lengths of PVC pipe and steel rod can be threaded together. To determine the sample collection depth, the outside of the sampling instrument will be graduated in .5-foot increments.

POND SOLIDS SAMPLING DEVICE

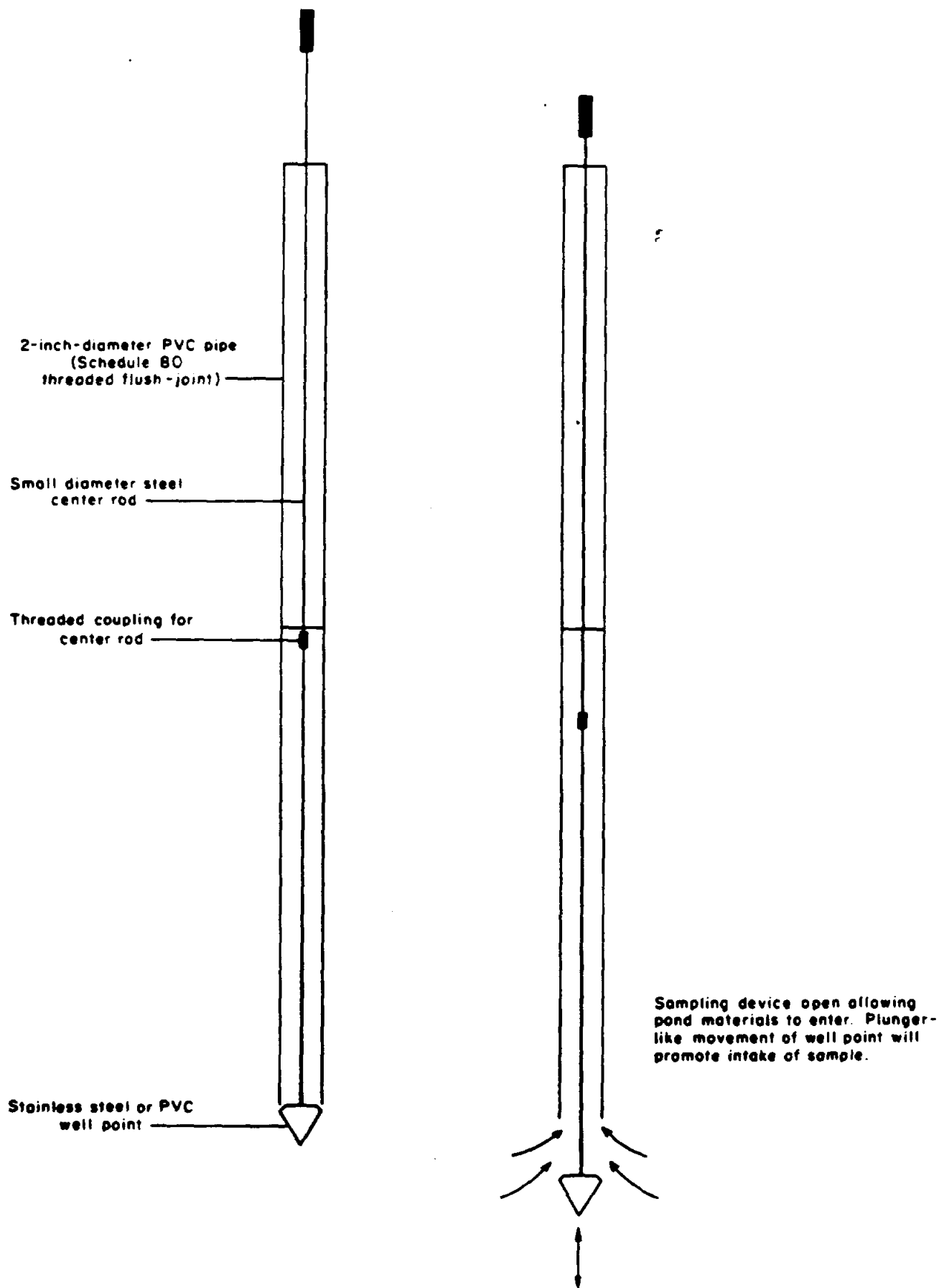


FIGURE 3.6-6 Conceptual design for device to be used in
collection of pond samples during Phase I RI

At each pond sampling location, after the uppermost sample has been collected, the hand-augered borehole will be advanced through the solid upper layer into the oozy sludge. With the bottom plug of the sampling device in the closed position (see Figure 3.6-6), the tube will be pushed to the desired sampling depth, as determined by one foot increments marked on the outside of the instrument. At the selected sampling depth, the bottom plug of the tube will be opened by pushing down on the steel center rod, allowing sludge to flow up into the device (see Figure 3.6-6). To encourage sludge intake into the tube, the steel rod and bottom plug can be worked up and down, with a plunger-like action. The bottom plug of the device will then be closed and the sampling device pulled from the borehole.

In any given pond or pond section, the samples from the pond surface at each designated location will be collected first. The individual samples (approximately one liter each) will be combined in a common glass container which will be kept on ice. After samples from a given sampling interval have been collected, they will ~~be combined~~ slowly to form a composite sample. The blending container will be fitted with an air-tight lid or cover to reduce sample degassing and to prevent possible cross-contamination via airborne particulates. The appropriate sample containers (see Table 3.6-3) will then be filled from the composite.

These composite samples will be subjected to analyses for the parameters provided in Table 2.2.1. Replicate pond solids samples will be prepared and submitted for analyses at a rate of 10 percent (5 replicates will be prepared). Due to the sample matrix, no field blank or trip blank will be prepared.

The composited samples shall be tightly packed into the sample jar in order to minimize air space and the potential for degassing. The sample jars will be labeled to indicate the retention pond number and section, the sample depth interval, the number of individual samples comprising the composite, date, and the names of the sampling personnel. All samples will be held in a cooler chest and cooled to about 4°C following collection. Following completion of sampling, the samples shall be forwarded to the selected laboratory using the chain-of-custody procedures described in Section 3.7 of this QAPP. All unused pond solids shall be returned to the pond or pond section from which they were collected.

One bucket auger, equipped with a stainless steel collection barrel, and up to four sludge sampling instruments will be used during the pond sampling task (i.e., one sludge sampling device shall be assigned for use at each sampling location within a given pond or pond section). The bucket auger will be washed with Sparkleen soap solution and rinsed with clean water between

sampling locations. Following collection of individual sludge samples from a given depth at each location within a pond or pond section, the sample collection devices shall be steam cleaned with a Sparkleen soap solution before being used to gather samples from the next sampling depth. The steam cleaning of the sludge sampling device will be performed at the washdown area described in Section 3.6.1.3. The runoff water resulting from the disposal pond sampling program will be collected in a separate holding tank. This water will then be sampled and analyzed according to Section 3.6.1.3 and an appropriate disposal method selected.

Following completion of sampling activities in each pond or pond section, the sample locations will be marked with a wooden stake driven into the pond surface. The stake will be labeled to indicate the borehole designation (e.g., Pond 5, Section A, #1) and the date. The approximate locations of the sampling locations will be determined by project field personnel using a Brunton compass and 300-foot nylon measuring tape.

To assess the permeability of the disposal pond surfaces, a double ring infiltrometer test will be performed near the center of each pond or pond section. The infiltrometer tests will be conducted according to ASTM Method D 3385-75. This procedure is provided at the end of this section.

3.6.3 Carbon Runoff Area Sampling/Boring Procedures

As outlined in Section 2.7, two samples of carbon material and underlying soil shall be collected from each of three identified deposition areas south of Ponds 1 and 2 (see Figure 2.7-1). Samples shall be collected from a depth just above the contact with underlying soil. This should provide a sample that has been subjected to less extensive leaching than near-surface materials. In order to avoid over coring and possible cross-contamination during the collection of the carbon material and underlying soil, the depth from which the sample is to be collected shall be determined by conducting a preliminary boring to determine the depth to natural soils. ~~The sample of the~~ carbon material and underlying soil will ~~be collected~~ using a hand augering device equipped with a ~~three-inch-diameter~~ collection barrel (stainless steel construction). Prior to collecting each sample, the sampling device shall be cleaned with Micro solution and rinsed with tap water, then with distilled water.

Because sampling of the underlying soil through the same corehole from which the sample of carbon material was collected could potentially cross-contaminate the soil sample, an area several feet across shall be excavated (with a hand shovel) down to and slightly below the contact with the underlying soil. This

is to provide direct access to the underlying soil and should prevent loose carbon material from falling onto the hole from which the sample of the underlying soil is to be collected. The hand auger sampling device will then be cleaned as indicated above and used to advance a borehole until natural soil is encountered that is free of particle carbon that may have migrated downward from the overlying deposits. This determination will be made by the G&M field geologist, based on visual inspection of the soils. The hand auger will then be recleaned and lowered into the pilot hole to collect a soil-sample which will be submitted for laboratory analysis. A conceptual depiction of the sampling procedure is provided in Figure 3.6-7.

It is anticipated, based on previous site investigations, that the soil material beneath the carbon deposits will be a soft to medium-stiff clay. In this type of material, there should be no difficulty in advancing the hand auger to the required sampling depth. ~~If circumstances do arise that require the use of power ~~drill~~ sampling tools,~~ any necessary alterations to the sampling program will be noted in the sampling log and also in the daily log.

The sample of carbon material and the sample of underlying soil shall be placed directly into the appropriate sample containers (see Table 3.6-3) and packed tightly in order to

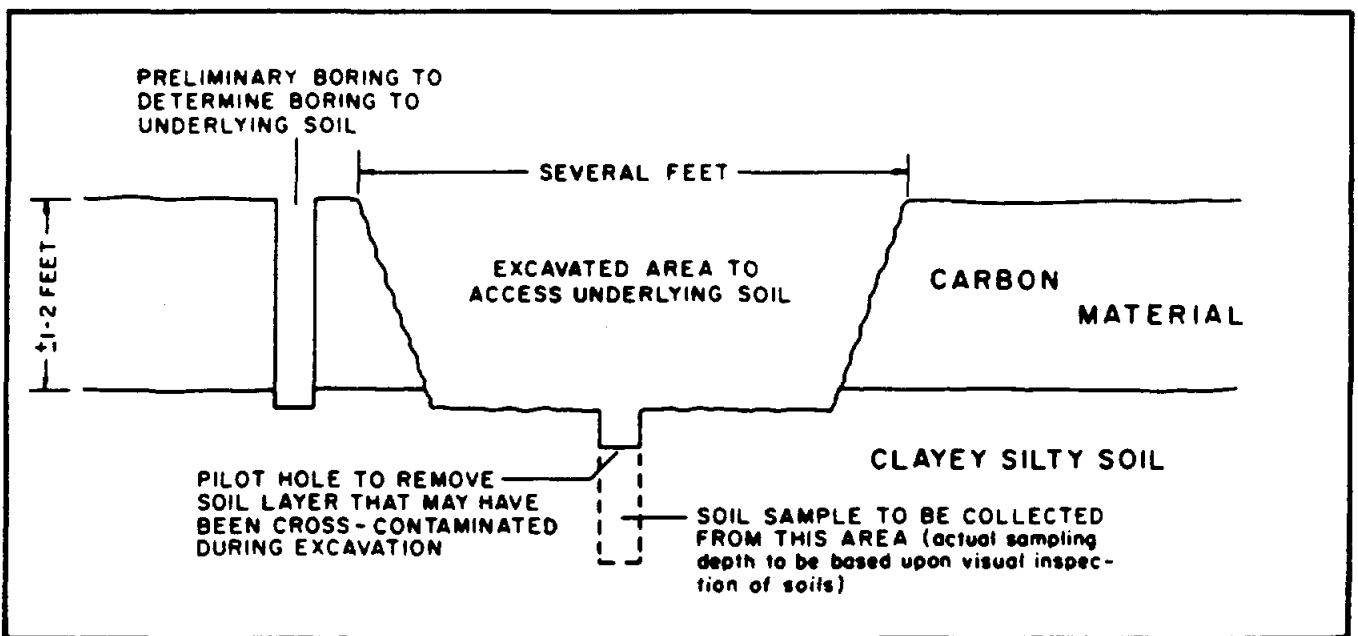
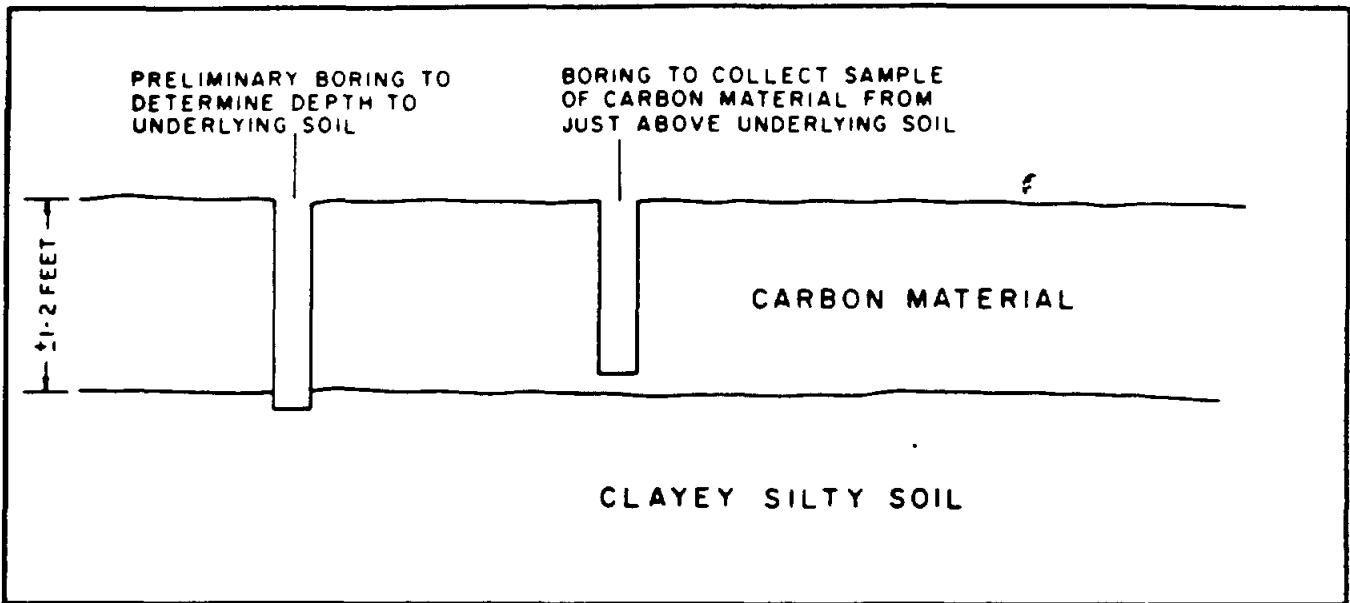


FIGURE 3.6-7. Generalized method to be used in collecting samples from carbon deposition areas and underlying soils.

minimize air space and the potential for degassing. The sample jars shall be labeled to show sample identification number, date, depth of collection, and the name(s) of sampling personnel. The samples shall be kept in a cooler chest and chilled to approximately 4°C following collection. At the time of sampling, a diagram will be prepared to indicate the location from which the sample was taken and a wooden stake will be driven at the sample collection point and labeled with the sample numbers and date of collection. The cored hole into the underlying soil shall then be backfilled with bentonite powder and any excess carbon material removed during the sample collection procedure shall be tamped back into the hand-dug excavation. Following completion of sampling, the samples shall be forwarded to the approved laboratory using the standard chain-of-custody procedures outlined in Section 3.7. One replicate carbon sample and one replicate sample of the underlying soil will be prepared and submitted for analysis. No trip blank or field blank will be utilized.

In ~~addition to~~ collecting samples from the three areas of carbon deposition and the underlying soils, the wooded area where the deposits are located will be gridded off into 50' x 50' sections (see Section 2.7). The grid will be established using a Brunton compass and a 300-foot nylon surveyor's tape.

A shallow hand soil boring shall be advanced approximately six (6) inches into natural soil at the intersection of each grid line. Carbon and soil samples will be inspected and described in the field for gross composition, texture, thickness of carbon material, depth to carbon/soil contact and other observable physical properties in accordance with procedures outlined in Section 3.6.1. A composite sample of the soil material encountered will be retained in a glass sample jar with a water-tight lid. The jar will be labeled to indicate sample depth interval, grid-mark designation, date of collection, and the name of the field geologist (see Section 3.6.1 for standard soil sample handling procedures).

Each of the sampling locations will be marked with a wooden stake identifying the grid-mark designation and the date.

3.6.4 River Sediment Sampling Procedures

According to Section 2.4, samples of the Ohio River sediment are to be collected at six locations as indicated on Figure 2.4-1.

Sediment samples shall be collected from the surface of the sediment to a depth of not more than one (1) foot. This is to obtain a sample most representative of current or near-recent depositional conditions. Sediment samples shall be collected

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DEC 2 1987

Section No. 3.6
 Revision No. 2
 Date: 9-21-87
 Page 22 of 38

ENVIRONMENT SERVICES DIVISION

using a hand augering device equipped with a three-inch-diameter collection barrel (stainless steel construction). Approximately one liter of whole sample (sediment and water) shall be collected at each of the sampling locations. In the event that a large quantity of gravel and/or organic material is collected in the sample, that sample will be discarded and a second sample will be collected several feet from the previous sampling location. The sampling device shall be cleaned with Sparkleen solution and rinsed with tap water, then distilled water prior to sampling at each location.

Each sample shall be placed directly into the appropriate sample jars (see Table 3.6-3), with the sediment being tightly packed into the container in order to minimize air space and the potential for degassing. The sample jar shall be labeled to show sample identification number, date, and the name(s) of sampling personnel. All sediment samples shall be kept in a cooler chest and chilled at approximately 4° C following collection. At the time of sampling, a diagram will be prepared and a marker stake shall be placed on the river bank to indicate the location from which each sample was collected. Following completion of sampling, river-sediment samples shall be forwarded to the selected laboratory using the standard chain-of-custody procedures provided in Section 3.7. One replicate sample of river sediment will be collected and submitted for analysis.

3.6.5 Ground-water Sampling Procedures

DEC 2 1987

ENVIRONMENT SERVICES DIVISION

During ground-water and seep sampling activities, a monitoring well sampling checklist (Figure 3.6-8) shall be filled out on a daily basis. This form documents various aspects of the sampling procedures which can effect data quality and validity.

Measuring Water Levels

Prior to bailing, purging, and sampling, the static water level in the well will be measured and the volume of standing water in the well must be calculated. Where a number of monitoring wells are to be sampled, a full round of water levels shall be taken prior to starting the water sampling.

The advantages of doing this are: 1) it provides potentially more accurate data for water table maps, relative to measurements collected over a period of days; 2) it allows the sampling team to become oriented to a new site; and 3) it provides the sampling team with immediate information about unusual circumstances such as wells that might be lost, damaged, dry, or inaccessible. If it becomes apparent that a well cannot be sampled, the sampling plan shall be modified accordingly and the G&M Project Manager notified. Any such changes shall be noted in the field log book.



SAMPLING OF MONITORING WELLS DAILY CHECKLIST

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DEC 2 1987

PROJECT: _____

WELL(S): _____

LOCATION: _____

DATE: _____

G&M PERSONNEL ON SITE: _____

TIME: _____

CHECKED BY: _____

ITEMS	OK/NA	COMMENTS
PRIOR TO SAMPLING:		
Health & safety precautions (HASP) received; equipment ready		
Sample containers, coolers, received from laboratory; ice or ice packs ready		
Sampling equipment and supplies inventoried, clean, and operational		
Checked in with client at site.		
Integrity of well noted		
Well area prepared for sampling; plastic placed around well; gasoline-powered pumps placed downwind.		
Well and water-level measurements made and recorded along with other pertinent field information on water sampling log.		
Field instruments calibrated.		
Sample containers labelled; preservatives added, if necessary.		
DURING AND AFTER SAMPLING:		
Well purged three to five times its volume		
Sample collected using a bailer or pump as per sampling plan.		
Measurement of field parameters recorded on sampling log.		
Sample containers filled according to collection protocol of analyses.		
Field and trip blanks collected; replicates or split samples collected as per sampling plan.		
Samples stored at 4°C in coolers for transport to lab.		
Water sampling log and chain-of-custody form completed.		
Reusable equipment decontaminated; non-reusable equipment disposed of in appropriate manner.		
Well secured and locked.		
Laboratory contacted to confirm receipt and condition of samples		
Additional Comments:		

FIGURE 3.6-8 Daily checklist for conducting ground-water and seep sampling activities

The volume of water purged from the well will be calculated directly by using a container of known volume. The rate of flow, in gallons per minute, will be measured by recording the time (via stopwatch) required to fill the container. The rate and volume of water evacuated from the well will be noted on the Water Sampling Log.

QUALITY ASSURANCE BRANCH
DEC 2 1987

ENVIRONMENT SERVICES DIV

Well evacuations shall be accomplished using a bladder-type submersible pump or Teflon bailer. Gas-operated bladder pumps consist principally of a collapsible membrane inside a long, rigid housing, with a compressed gas supply and appropriate control valve. When the pump is submerged, water enters the collapsible membrane through the bottom check valve. After the membrane has filled, gas pressure is applied to the annular space between the rigid housing and membrane, forcing the water upward through a sampling tube. When the pressure is released, the top check valve prevents the sample from flowing back down the discharge line, and water from the well again enters the pump through the bottom check valve.

Well Sampling Procedure

Well-water samples will be collected using Teflon bottom-filling bailers which will be cleaned immediately prior to use. Cleaning will include washing with Sparkleen solution, a tap water rinse and a distilled water rinse.

For purposes of quality control, we regard the field cleaning of bailers to be preferable to precleaning in a laboratory for three reasons:

QUALITY ASSURANCE BRANCH

DEC, 2 1987

ENVIRONMENT SERVICES DIVISION

1. Contaminants present in the laboratory or wrapping materials may enter the bailer.
2. Residues may be introduced during transit to the site.
3. It is generally not possible for all interested parties to observe laboratory cleaning, wrapping, and transport protocols.

The efficiency of the field cleaning protocols will be monitored by the use of random field blanks, where laboratory pure water will be run through newly cleaned bailers just prior to sampling. Replicate samples comprising about 10 percent of the total sample set shall be collected throughout the sampling program. Trip blanks will be prepared at a rate of one per shipment and field blanks will be prepared at a rate of one per day.

If a well will not yield the volume of water necessary to immediately fill the required number of sample containers, the filled and partially filled containers will be tightly capped, kept out of sunlight and cooled to approximately 4°C, until the necessary volume of samples can be obtained.

NOV 24 1987

ENVIRONMENT SERVICES DIVISION

Sample Preparation

Once samples have been collected they shall be prepared and held in accordance with the outlined requirements specified in Table 3.6-2. Only those water samples designated for metals analyses requiring acid preservation shall be filtered. This is to remove the suspended material in the sample (e.g., silt and clay), which could be digested by the acid, resulting in elevated levels of those metals that are naturally occurring constituents of the silt and clay. Filtration will be through a fiberglass prefilter prior to being preserved. Because the alluvial aquifer beneath the Ormet facility is relatively permeable, colloids (e.g., silica-related) and other very fine particles are believed to be actually moving with the ground water. Filtration through a 0.45 micron membrane filter could remove some of these constituents, resulting in a less accurate characterization of aquifer conditions. Also, relatively affected ground-water samples (characterized by a dark tea to coffee color) will not readily pass through 0.45 micron membrane filters, and the dilution that can occur as a result of repeatedly changing the filters and rinsing the device could diminish the representativeness of the sample.

Water samples designated for cyanide analysis will be tested in the field for the presence of sulfide and oxidizing agents. If these constituents are detected, they will be removed prior to

DEC 18 1987

ENVIRONMENT SERVICES DIVISION

TABLE 3.6-2

PARAMETERS TO BE ANALYZED FOR AND LABORATORY METHODS
TO BE USED IN GROUND-WATER AND SEEP ANALYSES

ANALYTICAL PARAMETER	CONTAINER TYPE	PRESERVATIVE	HOLDING TIME	VOL. ML.	METHOD
		(1, 2, 3)	MAXIMUM (4)		
Field Temperature	Plastic or Glass	NONE	NONE	---	See Section 3.6.5
Field pH	Plastic or Glass	NONE	NONE	---	See Section 3.6.5
Field Conductivity	Plastic or Glass	NONE	NONE	---	See Section 3.6.5
pH (Lab)	Plastic or Glass	COOL 4° C	6 hrs.	50	EPA 150.1
Conductance (Specific)	Plastic or Glass	COOL 4° C	28 days	100	EPA 120.1
Solids (Dissolved)	Plastic or Glass	COOL 4° C	7 days	100	EPA 160.1
Solids (Suspended)	Plastic or Glass	COOL 4° C	7 days	100	EPA 160.2
Alkalinity	Plastic or Glass	COOL 4° C	14 days	100	EPA 310.1
Silica	Plastic	COOL 4° C	28 days	50	EPA 370.1
Chloride	Plastic or Glass	COOL 4° C	28 days	100	EPA 325.3
Fluoride	Plastic	COOL 4° C	28 days	300	EPA 340.2
Sulfate	Plastic or Glass	COOL 4° C	28 days	50	EPA 375.4
Ammonia-Nitrogen	Plastic or Glass	H ₂ SO ₄ (pH<2)	28 days	400	EPA 350.2
Cyanide (Total)	Plastic or Glass	NaOH (pH>12)	14 days	50	CLP PROTOCOL (5)
Cyanide (Amenable to Chlorination)	Plastic or Glass	NaOH (pH>12)	14 days	50	EPA 335.1
Sodium	Plastic or Glass	HNO ₃ (pH<2)	6 mos.	100	SW846/7770
Potassium	Plastic or Glass	HNO ₃ (pH<2)	6 mos.	100	CLP PROTOCOL (5)
Calcium (by atomic absorption)	Plastic or Glass	HNO ₃ (pH<2)	6 mos.	100	SW846/7140
Aluminum	Plastic or Glass	HNO ₃ (pH<2)	6 mos.	50	CLP PROTOCOL (5)
Magnesium (by atomic absorption)	Plastic or Glass	HNO ₃ (pH<2)	6 mos.	100	CLP PROTOCOL (5)
Iron (total)	Plastic or Glass	HNO ₃ (pH<2)	6 mos.	100	CLP PROTOCOL (5)
Manganese	Plastic or Glass	HNO ₃ (pH<2)	6 mos.	50	CLP PROTOCOL (5)
Zinc	Plastic or Glass	HNO ₃ (pH<2)	6 mos.	100	CLP PROTOCOL (5)
Copper	Plastic or Glass	HNO ₃ (pH<2)	6 mos.	100	CLP PROTOCOL (5)
Nickel	Plastic or Glass	HNO ₃ (pH<2)	6 mos.	100	CLP PROTOCOL (5)
Cobalt	Plastic or Glass	HNO ₃ (pH<2)	6 mos.	100	CLP PROTOCOL (5)
Chromium (total)	Plastic or Glass	HNO ₃ (pH<2)	6 mos.	100	CLP PROTOCOL (5)
Lead	Plastic or Glass	HNO ₃ (pH<2)	6 mos.	100	CLP PROTOCOL (5)
Cadmium	Plastic or Glass	HNO ₃ (pH<2)	6 mos.	100	CLP PROTOCOL (5)
Barium	Plastic or Glass	HNO ₃ (pH<2)	6 mos.	100	CLP PROTOCOL (5)
Arsenic	Plastic or Glass	HNO ₃ (pH<2)	6 mos.	50	CLP PROTOCOL (5)
Mercury	Plastic or Glass	HNO ₃ (pH<2)	26 days	100	CLP PROTOCOL (5)
Selenium	Plastic or Glass	HNO ₃ (pH<2)	6 mos.	50	CLP PROTOCOL (5)
Silver	Plastic or Glass	HNO ₃ (pH<2)	6 mos.	50	CLP PROTOCOL (5)
Antimony	Plastic or Glass	HNO ₃ (pH<2)	6 mos.	50	CLP PROTOCOL (5)
Beryllium	Plastic or Glass	HNO ₃ (pH<2)	6 mos.	50	CLP PROTOCOL (5)
Thallium	Plastic or Glass	HNO ₃ (pH<2)	6 mos.	50	CLP PROTOCOL (5)
Tin	Plastic or Glass	HNO ₃ (pH<2)	6 mos.	50	EPA 282.1
Vanadium	Plastic or Glass	HNO ₃ (pH<2)	6 mos.	50	CLP PROTOCOL (5)
TOC (Total Organic Carbon)	Glass	H ₂ SO ₄ (pH<2)	28 days	10	EPA 415.1

DEC 18 1987

TABLE 3.6-2 (continued)

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ANALYTICAL PARAMETER	CONTAINER TYPE	PRESERVATIVE	HOLDING TIME	VOL. ML.	METHOD
		(1, 2, 3)	MAXIMUM (4)		
Volatile Organic Compounds	VOA	COOL 4° C	14 days	40	CLP PROTOCOLS (6)
Semi-Volatile Organic Compounds	Amber Glass	COOL 4° C	7 days	1000	CLP PROTOCOLS (6)
Pesticides and PCB	Amber Glass	COOL 4° C	7 days	2000	CLP PROTOCOLS (6)

Notes for Table 1:

- 1) Unless otherwise specified, all ground-water samples shall be kept cool at about 4° Centigrade (i.e., COOL 4°C), from the time of collection until delivery to the laboratory.
- 2) Sample preservation should be performed immediately upon sample collection. For composite chemical samples each aliquot should be preserved at the time of collection.
- 3) When any sample is to be shipped by common carrier or sent through the United States Mails, it must comply with the Department of Transportation Hazardous Material Regulations (49 CFR Part 172). The person offering such material for transportation is responsible for ensuring such compliance. For the preservation requirements of Table 3, the Office of Hazardous Materials, Materials Transportation Bureau, Department of Transportation has determined that the Hazardous Materials Regulations do not apply to the following materials: Hydrochloric acid (HCL) in water solutions at concentrations of 0.04% by weight or less (pH about 1.96 or greater); Nitric acid (HNO₃) in water solutions at concentrations of 0.15% by weight or less (pH about 1.62 or greater); Sulfuric acid (H₂SO₄) in water solutions at concentrations of 0.35% by weight or less (pH about 1.15 or greater); and Sodium hydroxide (NaOH) in water solutions at concentrations of 0.080% by weight or less (pH about 12.30 or less).
- 4) Samples should be analyzed as soon as possible after collection. The times listed are the maximum times that samples may be held before analysis and still be considered valid.
- 5) Analyses of CLP inorganic compounds shall be according to EPA 504 No. 786; 10-86 Rev. (IFB 68-01-7329).
- 6) Analyses of CLP organic compounds shall be according to IFB WA-87K236, WA-87K237, and WA-87K238.

TABLE 3.6-3

PACKAGING DETAILS FOR POND SOLIDS, SOILS,
CARBON MATERIAL AND RIVER SEDIMENT SAMPLES

SAMPLE MATRIX	TOTAL CONTAINERS	PARAMETER	CONTAINER TYPE	PRESERVATION	HOLDING TIME	METHOD
Disposal Pond Solids	4-1 pt. plastic 6-8 oz. amber glass	VOA	Amber Glass	Cool 4°C	10 days	***
		Semi-volatiles	Amber Glass	Cool 4°C	10 days/40 days*	***
		Metals	Plastic	Cool 4°C	6 mos.	***
		Cyanide	Plastic	Cool 4°C	14 days	***
		Mercury	Plastic	Cool 4°C	26 days	***
		Other Inorganics	Plastic	Cool 4°C	**	***
Potliner Area Solids	1-1 qt. plastic 1-1 qt. amber glass 1-8 oz. amber glass	VOA	Amber Glass	Cool 4°C	10 days	***
		Semi-volatiles	Amber Glass	Cool 4°C	10 days/40 days*	***
		Metals	Plastic	Cool 4°C	6 mos.	***
		Cyanide	Plastic	Cool 4°C	14 days	***
		Mercury	Plastic	Cool 4°C	26 days	***
		Other Inorganics	Plastic	Cool 4°C	**	***
River Sediments	4-1 qt. plastic 6-8 oz. amber glass	VOA	Amber Glass	Cool 4°C	10 days	***
		Semi-volatiles	Amber Glass	Cool 4°C	10 days/40 days*	***
		Metals	Plastic	Cool 4°C	6 mos.	***
		Cyanide	Plastic	Cool 4°C	14 days	***
		Mercury	Plastic	Cool 4°C	26 days	***
		Other Inorganics	Plastic	Cool 4°C	**	***
Carbon Material	6-1 pt. plastic 6-8 oz. amber glass	VOA	Amber Glass	Cool 4°C	10 days	***
		Semi-volatiles	Amber Glass	Cool 4°C	10 days/40 days*	***
		Metals	Plastic	Cool 4°C	6 mos.	***
		Cyanide	Plastic	Cool 4°C	14 days	***
		Mercury	Plastic	Cool 4°C	26 days	***
		Other Inorganics	Plastic	Cool 4°C	**	***

TABLE 3.6-3 (continued)

PACKAGING DETAILS FOR POND SOLIDS, SOILS,
CARBON MATERIAL AND RIVER SEDIMENT SAMPLES

SAMPLE MATRIX	TOTAL CONTAINERS	PARAMETER	CONTAINER TYPE	PRESERVATION	HOLDING TIME	METHOD
Soils Beneath Carbon Deposits	6-1 pt. plastic 6-8 oz. amber glass	VOA	Amber Glass	Cool 4°C	10 days	***
		Semi-volatiles	Amber Glass	Cool 4°C	10 days/40 days*	***
		Metals	Plastic	Cool 4°C	6 mos.	***
		Cyanide	Plastic	Cool 4°C	14 days	***
		Mercury	Plastic	Cool 4°C	26 days	***
		Other Inorganics	Plastic	Cool 4°C	**	***

* - Semi-volatiles must be extracted within 10 days, analyses must then be performed within an additional 40 days

** - Holding times for non-CLP inorganics in soils, sludges, etc. will be in accordance with holding times for those parameters in water (see Table 3.6-2)

*** - Analyses shall be by approved EPA methods. For CLP organic parameters, analyses shall be according to IFB WA-87K236, WA-87K237, and WA-87K238. Analyses of CLP inorganic parameters shall be according to EPA SOW No. 786; 10-86 Rev. (IFB 68-01-7329).

DEC 16 1987

DEC 16 1987

DEC 16 1987

preservation with sodium hydroxide. The procedures for conducting these field analyses are provided in Reference 5 at the end of this QAPP.

It should be noted that only those samples to be submitted for metals analyses will be filtered. All samples shall be preserved in accordance with the Manual of Ground-Water Sampling Procedures (Scalf and others, 1981) or as otherwise specified by the laboratory selected to perform the water-quality analyses. Preservatives to be used in fixing ground-water samples for the various chemical analyses to be conducted are included in Table 3.6-2.

Following sample preparation, all ground-water samples shall be kept in cooler chests at a temperature of approximately 4°C until they are delivered to the water-testing laboratory. Chain-of-custody procedures and other shipping protocols are further discussed in Section 3.7.

Procedures for Conducting Field Analyses

Measurements for pH, temperature, and specific conductance shall be made in the field at the time of sampling because these chemical properties are difficult to preserve during storage. No holding time is permissible. Approximately one half-gallon of

sample will be placed in a clean, unpreserved glass container when field measurements are conducted. Field measurements will be recorded in the G&M Water Sampling Log (see Figure 3.6.-9).

Temperature:

Temperature will be measured with a rapidly equilibrating, mercury-filled Celsius thermometer, immediately following collection of the sample.

pH:

The pH shall be determined with a glass hydrogen ion electrode compared against a reference electrode of known potential by means of a pH meter or other potential measuring device with a high input impedance. Because pH is exponentially related to concentration, care must be exercised in making a measurement.

Measurement of pH is temperature-sensitive, so the standard buffers should be at a temperature near that of the sample for precise determinations. This can be accomplished by immersing a bottle or test tube containing buffer in the sample discharge.

The pH meter shall be calibrated at the beginning of any sampling day. Calibration is standard two-buffer calibration, following manufacturers' instructions which are included in

Section 3.8. Commonly available buffers have nominal pH values of 4, 7 (sometimes 6.86), and 10. The two buffers that are most likely to bracket the sample pH values shall be used. A one-point calibration (pH 7) will be made each time the unit is moved. Buffer solution shall be decanted from the storage bottle to a small beaker or tube for calibration and then discarded.

Before a measurement is made, the probe is completely rinsed with a stream of deionized or distilled water. Then, to measure pH, the probe is lowered into a container of sample water and allowed to equilibrate. To facilitate equilibration, the probe is used to gently stir the water. (Gentle stirring helps minimize sample aeration.) A pH reading is made as soon as the reading on the meter steadies. Between measurements, the probe will be immersed in deionized water or buffer. At least a one-point calibration shall be performed prior to measuring pH in each sample.

Specific Conductance:

The ability of a solution to conduct an electrical current is a function of the concentration and charge of the ions in solution and the rate at which the ions can move under the influence of an electrical potential. A battery-powered conductivity meter will be used to take the specific conductance measurements. The probe shall be kept clean, and calibrated daily with a conductivity standard, (see Section 3.8).

To measure the sample's specific conductance, the probe will be lowered into the sample and stirred gently. A reading shall be taken within seconds after immersion. Before and after each use, the probe shall be cleaned with a stream of deionized or distilled water.

Recording of Field Data and Labeling of Samples

Field Log Book:

A bound notebook will be used by the field team for recording all sampling events and field observations. Entries in the log book shall be dated and signed by the person making the entry. The log book will be kept in a secure dry place. Entries may not be made in water-soluble ink. The type of information to be included in the log is:

Date
Client
Location
Weather
Sample crew
Work progress
Control samples

Any information that is not normally recorded on the G&M logs and forms should also be included in the Log Book, e.g.,

Delays
Unusual situations
Well damage
Departure from established QA/QC field procedures
Instrument problems
Accidents

The sampling team shall also maintain the Water Sampling Logs, kept in a ring binder, to record information about each sample collected. The Log will be completed at the time of sampling. It will provide documentation to indicate that sampling requirements have been met. The standard Water Sampling Log is shown in Figure 3.6-9. It includes, in addition to project information and well evacuation data, the following information on sampling:

- Physical appearance of samples
- Field observations

- Results of field analysis
- Sampling methods and materials
- Constituents sampled
- Sample container and preservation
- Sampling personnel

Sample Labels:

Sample labels are necessary to identify and prevent misidentification of the samples. The labels shall be affixed to the sample containers (not the caps) prior to the time of sampling. The labels shall be filled out in pencil at the time of collection. The labels should include the following information:

- Sample number
- Name of collector
- Date and time of collection
- Client and geographic location
- Geraghty & Miller
- G&M project number

After marking, the labels will be covered with clear acetate tape for protection. An example of the sample label to be used is provided in Figure 3.6.-10.



Sample I.D.: _____

Sample Type: ☐ Grab ☐ Composite

Sample Medium: _____

Date: _____ Time: _____

Analysis Requested: _____

Preservative: _____

Sampled By: _____

FIGURE 3.6-10 Standard sample identification label
for use on ground-water and seep sample
containers.

3.6.6 Procedures for Collecting and Packaging Seep Samples

Collection and Packaging Procedures:

Seep samples shall be collected via a standard grab-sampling technique with fluids being collected as close as possible to the points of issuance. Depending upon the occurrence of the seep (i.e., minimal flow across the surface of the ground), it may be necessary to modify this proposed sampling procedure in order to permit efficient sample collection and to obtain the required sample volume. If seep flow is limited to preclude direct grab-sampling, a shoven (properly cleaned with Sparkleen soap and a distilled water rinse) will be used to create a small reservoir to facilitate sample collection. In the event that the reservoir must be left for a period of time to recharge, it will be covered with plastic to prevent possible cross-contamination by airborne particulates. Regardless of the technique used, adequate circulation and outflow shall (to the extent possible) be maintained to avoid stagnation of the water in order to prevent major changes in temperature and/or the possible reaction of certain constituents with prolonged exposure to air and/or sunlight. All tools and materials used in the modification of the seep (if necessary) shall be cleaned with a soap and water wash and a distilled water rinse prior to and after use.

In order to allow any suspended sediments that may result from the seep modification process to settle out, the modified seep shall be left for a period of at least one (1) hour before water samples are collected; assuming that creation of a reservoir is necessary. At the end of this time, a peristaltic pump shall be used to collect the water sample from the holding reservoir. If adequate flow is occurring at the collection point, samples shall be collected directly via the standard grab-sampling technique.

If flow is very limited, a longer period of time may be required to obtain adequate sample volumes. In this case, the filled and partially filled sample containers shall be kept cool approximately (4°C) and out of direct sunlight until an adequate volume of fluid has been collected. Sample filtering and preservation techniques will be similar to those applied to ground-water samples, as outlined in Section 3.6.5. Standard forms for logging water-sampling data and results of field analyses; procedures for conducting field analyses, recording field data, and labeling of samples; and chain-of-custody procedures shall be in general accordance with those outlined in Section 3.6.5 addressing ground-water sampling protocols.

QUALITY ASSURANCE BRANCH

DEC 18 1987

3.6.7 Air Monitoring Procedures

Because several of the Ormet process facilities, which sometimes generate dust, are situated generally upwind from the suspected source areas, the air sampling stations must be properly located so that process-related particulate can be differentiated from airborne dust originating within the suspected source area. The final selection of appropriate locations for the upwind air samplers has been made following completion of the assessment of wind-flow patterns at the Ormet facility, and are shown in Figure 2.8-6.

Ormet has contracted Energy & Environmental Management Inc. (E²M) to conduct the air monitoring program.

Two air samplers shall be installed at locations upwind from the suspected source areas to characterize the amount of respirable particulate (less than 10 micron) present in the wind prior to its passage over the suspected source area; i.e., to characterize back-ground wind conditions. Two additional air samplers will also be established at locations downwind from the suspected source areas in order to assess the amount of respirable wind-borne dust emanating from within these areas.

Twenty four (24) hour samples will be collected from each high-volume type sampler once every six (6) days for ten (10)

GERAGHTY & MILLER, INC.

QUALITY ASSURANCE PLAN

DEC 18 1987

Section No. 3.6
Revision No. 3
Date: 12-11-87
Page 38 of 38

ENVIRONMENTAL SCIENCE & TECHNOLOGY

months, for a total of 50 samples per sampler. The samples shall be analyzed for amount of respirable dust (PM_{10}) per unit volume air by a qualified independent laboratory, Hazen Research, Inc. of Golden, Colorado.

High-volume samplers manufactured by General Metal Works Corp. retrofitted with General Metal Works Model GMW-1200 PM_{10} Size-Selective Inlets shall be used. Filters shall be GMW-RN-100 Glass Micro-fiber High Purity Filters.

Filters will be removed from the samplers after each sampling period and mailed to Hazen Research for weighing. Pre-weights and post-weights are transmitted by Hazen to E^2M who will calculate the concentration of respirable dust in micrograms per cubic meter of air.

Detailed operations and quality assurance procedures to be followed by E^2M , Ormet, and Hazen Research personnel are included as Reference 6.

3.7 SAMPLE CUSTODY

Sample custody procedures are designed to provide documentation of preparation, handling, storage, and shipping of all samples collected during this project. Samples collected during the site investigation will be the responsibility of identified persons from the time the empty sample containers leave the laboratory, until the collected samples are analyzed.

3.7.1 Sample Container Inventory

Prior to each sampling event, a Sample Container Inventory Form (Figure 3.7-1) along with G & M chain-of-custody seals (Figure 3.7-2) will be forwarded to the laboratory. Using the inventory form, laboratory personnel will prepare a detailed inventory of all empty sample bottles being supplied to the site, including the number of bottles, bottle size, and the preservative (if any), included in each bottle. Each empty sample bottle will be sealed with a G&M seal, showing the signature of the laboratory personnel preparing the bottles for shipment. The inventory form will be signed and dated by the laboratory personnel preparing the shipment and also by the courier transporting the bottles to the site.

Once the shipment is received at the site, a member of the sampling team will sign and date the inventory form acknowledging



Project _____

Shipped to _____

Attn. _____

SHIPMENT CONTENTS

[illegible]

Received by _____

Date _____

Inspected by _____

Date _____

Seal Intact? _____

Remarks:

FIGURE 3.7-1 Standard form for tracking empty sample containers from the laboratory.

FIGURE 3.7-2 Examples of chain-of-custody seals to be utilized during sample transport to the laboratory

CHAIN-OF-CUSTODY SEAL

Geraghty & Miller, Inc.

CHAIN-OF-CUSTODY SEAL

CHAIN-OF-CUSTODY SEAL

Geraghty & Miller, Inc.

CHAIN-OF-CUSTODY SEAL

CHAIN-OF-CUSTODY SEAL

Geraghty & Miller, Inc.

CHAIN-OF-CUSTODY SEAL

CHAIN-OF-CUSTODY SEAL

Geraghty & Miller, Inc.

CHAIN-OF-CUSTODY SEAL

receipt of the shipment. The shipment will then be unpacked and the Sample Container Inventory Form checked against the contents of the shipment. All seals will be inspected to confirm their integrity. Any comments regarding the shipment will be noted and the inventory form signed and dated by the field personnel performing the inspection.

3.7.2 Field Custody

The sampling personnel are personally responsible for the care and custody of the samples collected until they are personally delivered to the analyzing laboratory or entrusted to a courier.

Chain-of-custody sample forms (Figure 3.7-3) will be completed prior to sample shipment. They will include the following information: sample number, time collected, date collected, source of sample, preservative, and name of sampler. These forms will be completed using waterproof ink and signed by the sampler. Similar information will be provided on the sample label, which is securely attached to the sample bottle. Each bottle will be sealed with a G&M custody seal (Figure 3.7-2). One chain-of-custody form will be completed for each shipping container being sent to the laboratory.

Project Number _____

Project Location: _____

Laboratory _____

Sampler(s) _____

SAMPLE IDENTITY	Date Sampled
-----------------	--------------

SAMPLE BOTTLE / CONTAINER DESCRIPTION

TOTAL**Total No. of Bottles/
Containers**

Relinquished by: _____	Organization: _____	Date: ____/____/____	Time: _____	Seal Intact? Yes No N/A
Received by: _____	Organization: _____	Date: ____/____/____	Time: _____	
Relinquished by: _____	Organization: _____	Date: ____/____/____	Time: _____	Seal Intact? Yes No N/A
Received by: _____	Organization: _____	Date: ____/____/____	Time: _____	

Special Instructions/Remarks: _____

Delivery method: ☐ In Person ☐ Common Carrier _____ ☐ Lab Courier ☐ Other _____

QUALITY ASSURANCE DIVISION

3.7.3 Transfer of Custody and Shipment

NOV 24 1987

Each sample shipping container will be accompanied by a chain-of-custody record (Figure 3.7-3). The original record will accompany the shipment; and a copy will be retained by the sampling personnel. When transferring samples, the individuals relinquishing and receiving them will sign date, and note the time on the record. This record documents sample custody transfer from the sampler to the laboratory. After being signed by the courier, the field chain-of-custody record will be placed inside the shipping container in a sealed plastic envelope. Given the proximity of Kemron to the Ormet facility, it is anticipated that G & M personnel will deliver the samples directly to the laboratory on a daily basis, or, Kemron will supply a courier from their facility to pick up samples from the site each day. This will eliminate the need to utilize a commercial carrier, thus streamlining the chain-of-custody process.

After collection, samples requiring refrigeration will be promptly cooled to approximately 4°C and packaged in an insulated cooler for transport to the laboratory. Only shipping containers which meet applicable State and Federal Standards for safe shipment will be used. The shipping container will be sealed with at least four G&M custody seals (one on each side), so that any tampering may be detected.

3.7.4 Laboratory Custody

Once at the laboratory, Kemron's sample custodian will note whether or not the custody seals are intact and take custody of the samples by signing the chain-of-custody sheet. All samples will then be logged in and stored in refrigerated space. Kemron maintains its whole facility as a secure facility. All entrances are either locked or under constant surveillance. In addition, all refrigerated storage space is locked at night. Only management and the sample custodian have access to locked refrigerators.

All sample analyses will be completed at Kemron's Marietta facility with the exception of the CLP inorganics. Kemron will forward these samples to CompuChem laboratories in North Carolina for analyses. The chain-of-custody will be maintained throughout this transfer as both Kemron and CompuChem (A CLP lab) are familiar with necessary shipping practices. During this transfer, Federal Express, Inc. will be used and they will also maintain the chain-of-custody.

With respect to shipping, Kemron expects no breakage as both the metals and cyanide will be sampled in plastic containers. These containers will be shipped in KEM-KITS.

DEC 18 1987

Section No. 3.7
Revision No. 3
Date: 12-7-87
Page 5 of 5

. Finally, completed chain-of-custody sheets will accompany all sample reports. All shipping, logging, and chain-of-custody documents will accompany the final report as specified by CLP protocol.

3.7.5 Final Evidence File

The final evidence file for the RI shall be maintained by G&M in a secure, limited access area and under custody of the G&M Project Manager. The file shall include all data, logs, field notebooks, pictures, QA/QC audit reports, progress reports, and other relevant records generated during the RI. Specific data records and management procedures to be utilized by G&M, including a description of the document control system, are provided in Section 3.5 of this QAPP. Unless otherwise specified, Kemron shall maintain all laboratory-generated documents for a period of three years after completion of the project.

3.8 CALIBRATION PROCEDURES AND FREQUENCY

A calibration procedure establishes the relationship between a known calibration standard and the measurement of that standard by an instrument or analytical procedure.

Field equipment, including pH and specific conductivity meters organic vapor analyzers (OVA), and MSA Samplair Model A Pump (cyanide vapor monitoring) will be calibrated and operated in accordance with the manufacturers instructions and manuals. Operating and calibration instructions for these instruments are provided in Reference 4 at the end of this Plan. A log book will be kept documenting the calibration results for each field instrument. The log book will include date, standards, personnel, and results of calibration.

Any equipment used to detect unsafe or potentially dangerous conditions for personnel will be calibrated as recommended by the manufacturer. Equipment used to quantitatively measure environmental parameters (e.g., pH and conductivity) will be calibrated at a minimum of once a day by comparison to a commercially prepared calibration standard.

Calibration procedures for laboratory equipment will be performed in accordance with the standard operating procedures for Kemron and CompuChem, which comprise Section 3.9.

DEC 18 1987

Section No. 3.9
Revision No. 3
Date: 12-11-87
Page 1 of 2

ENVIRONMENT SERVICES (OPTION)

3.9 ANALYTICAL SERVICE

Kemron Environmental Services of Marietta, Ohio will perform the analyses for organic compounds, as well as the analyses for non-CLP inorganic compounds. Analyses for the inorganic parameters of the CLP List will be performed by CompuChem Laboratories of Research Triangle Park, North Carolina. The QA/QC procedures and protocols utilized by these laboratories are provided in the following sections.

Kemron will perform the analyses for the CLP organic parameters according to CLP protocols, as specified in IFB WA-87K236, WA-87K237, and WA-87K238. Analyses of all non-CLP parameters will be performed following Kemron's standard operating procedures. Kemron's SOP is provided in Section 3.9.1.

Compuchem will provide analyses for CLP inorganic parameters (metals and cyanide) using CLP protocol as outlined in EPA SOW No. 786; 10-86 Rev. (IFB 68-01-7329).

DEC 18 1987

GERAGHTY & MILLER, INC.

ENVIRONMENTAL SERVICES DIVISION

Section No. 3.9
Revision No. 3
Date: 12-11-87
Page 2 of 2

3.9.1 Standard Operating Procedures and Analytical Quality Assurance Program for Kemron Environmental Services

Analyses for non-CLP inorganic parameters shall be performed according to Kemron's SOP, as presented in the following pages of this section.

Kemron shall perform the analyses for the CLP organic parameters according to CLP protocols, as specified in IFB WA-87K236, WA-87K237, and WA-87K238. These protocols shall take precedence over the procedures outlined in Section 7.2 of Kemron's SOP. Because they are standard EPA approved methods, these procedures are referenced in this plan, rather than included in their entirety.

3.9.2 Contract Laboratory Program Statement of Work for CompuChem Laboratories

Compuchem will provide analyses for CLP inorganic parameters (metals and cyanide) using CLP protocols as outlined in EPA SOW No. 786; 10-86 REV. (IFB 68-01-7329). Because they are standard EPA approved methods, these procedures are referenced in this Plan, rather than included in their entirety.

3.10 QUALITY CONTROL PROCEDURES QUALITY ASSURANCE BRANCH

NOV 24 1987

ENVIRONMENT SERVICES DIVISION

3.10.1 Laboratory Quality Control Checks

Procedures for laboratory quality control checks to be utilized by Kemron are documented in Section 3.9.

3.10.2 Field Quality Control Checks

Quality control samples generated by G&M will include the collection of field replicates, the preparation of field blanks, and the use of trip blanks. To assess laboratory performance, replicates will be collected in the field and sent to the analytical laboratory at a frequency of about 10 percent of the sample set. The anticipated number of quality control samples to be generated during Phase I of the RI is summarized in Table 3.10-1

Trip blanks will be shipped along with water samples and will be analyzed at the same time as all other samples. Trip blanks will be utilized at a rate of one sample per shipment.

Field blanks will be prepared using rinse water from the ground-water sampling equipment, and will be analyzed to determine if the sampling procedures may be biasing the data.

GERAGHTY & MILLER, INC.

Section No. 3.10
Revision No. 1
Date: 6-17-87
Page 2 of 2

Field blanks will be prepared and submitted at a rate of one per day. Procedures for collecting these samples are discussed in Section 3.6.5.

TABLE 3.10-1

SUMMARY OF FIELD GENERATED QUALITY CONTROL SAMPLES

<u>Sampling Event</u>	<u>Sample Type</u>	<u>Actual Samples</u>	<u>Replicates</u>	<u>Field Blanks</u>	<u>Trip Blanks</u>	<u>Total Samples Generated</u>
Ground-water and Seep Sampling	Water	57-60	6	10	5-10	78-86
Pond solids Sampling	Pond Solids	45	5	-	-	50
Former Potliner Storage Area Characterization	Soils ¹	120	12	-	-	132
	Soils ²	20-40	2-4	-	-	22-44
River Sediment Sampling	Sediment & Water	6	1	-	-	7
Carbon Runoff and Deposition Area Characterization	Carbon Material	6	1	-	-	7
	Soil	6	1	-	-	7

¹ Soil samples to be analyzed for six inorganic indicator parameters

² Soil samples to be analyzed for complete CLP list

3.12 PREVENTIVE MAINTENANCE

Preventive maintenance on field equipment will be performed in accordance with procedures supplied by the manufacturer. The manufacturer's operating and maintenance manuals will be kept on site and reviewed by personnel involved in equipment use. Frequent calibration procedures, as outlined in Section 3.8. will be used as a means of determining the need for equipment maintenance.

The maintenance of laboratory equipment will be performed by the laboratory according to specified procedures outlined in Reference 6.

3.13 SPECIFIC ROUTINE PROCEDURES USED TO ASSESS DATA PRECISION, ACCURACY, AND COMPLETENESS

All data generated in this investigation will be assessed for its representativeness, accuracy, and precision. The completeness of the data will be determined by comparing the acquired data to the stated project objectives to see that the objectives are being met. The procedures utilized by the analyzing laboratories to determine data precision, accuracy, and completeness are described in Section 3.9. Additional checks on method precision will be performed using similar methods on field collected replicate samples. Accuracy will be assessed using laboratory spiked samples and laboratory field blanks.

The representativeness of the data will be assessed by first determining if the proper procedures and protocols were followed during the collection of the samples from which the data were generated. Any non-adherence to the procedures and protocols shall be evaluated to determine its potential effect, if any, on the data. Also, the data validation package supplied by the laboratory (as required under the Contract laboratory Program) for each sample analysis will be reviewed to determine if there may be any laboratory-related sources of error in data.

Precision and accuracy will be assessed using QC samples as outlined in Section 3.10. Precision will be examined using replicate samples and accuracy by using blanks and spiked

This methodology is summarized in Section 3.9.

3.14 CORRECTIVE ACTION

If the periodic quality-control audits detect unacceptable conditions or data, the G&M Project Director, G&M QA/QC Officer, and G&M Project Manager are responsible for developing and initiating appropriate changes or modifications. The condition or problem will be specifically identified, recorded in the appropriate field log or project file, investigated, and the cause determined. Then, changes or modifications will be initiated to eliminate the problem. These may include:

- Re-analyzing samples if holding time and sample volume permit,
- Resampling and re-analyzing,
- Evaluating and amending sampling and/or analytical procedures,
- Accepting data, while documenting a level of uncertainty.

Upon implementation of changes or modifications, their effectiveness will be established and elimination of the problem verified. Details regarding the changes or modifications implemented and the results will be documented and retained in the project file.

3.15 QA REPORTS TO MANAGEMENT

On a regular basis, the G&M QA/QC Officer will review all aspects of the implementation of this QAPP and prepare a summary report to the G&M Project Manager and G&M Project Director. Reviews will be performed at the completion of each field activity and reports will be completed at this time. These reports will include:

- Assessments of measurement data accuracy, precision, and completeness,
- Results of performance, systems, data, and instrument audits, and
- Any changes or modifications which need to be taken or are to be taken.

Any significant QA problems will be reported and identified, and options for changing or modifying the program can be discussed.

When taking a full round of water-level measurements, care must be taken to avoid cross contamination of wells. When necessary, separate tapes shall be used.

QUALITY ASSURANCE BRANCH

DEC 2 1987

At the Ormet facility, an electric measuring tape (calibrated to 0.05 foot) shall be used for water-level measurements. These measurements shall be recorded in the Water Sampling Log (see Figure 3.6-9). The probe of the electric tape shall be washed with Sparkleen solution and rinsed with distilled water prior to measuring each well. In making each measurement, the probe shall be lowered into the well until the indicator light and/or buzzer signals that water has been reached. The depth to water is then read directly off the calibrated tape at the top of the well casing. Water-level elevation relative to mean sea level is found by subtracting the depth to water from the casing top elevation.

ENVIRONMENT SERVICES DIVISION

Set-up for Sample Collection

Plastic sheeting shall be placed around the well to protect sampling equipment from potential contamination. The top of the well casing will be cleaned with a clean rag. Sampling in the rain is not encouraged, but may be done if the vehicle can be located near enough and shelter (plastic sheeting) can be

constructed over the sample- handling area to minimize sample exposure. The preliminary information requested in the G&M Water Sampling Log (i.e., project, location, time, date, weather, etc.), shown in Figure 3.6-9 will be recorded at this time.

QUALITY ASSURANCE BRANCH

DEC 2 1987

Purging the Well

ENVIRONMENT SERVICES DIVISION

Standing water shall be removed from the well casing prior to collecting ground-water samples. Three (3) times the calculated volume of water in the well will be removed to ensure that a representative water sample is obtained from the aquifer. Wells that go dry during evacuation are sampled after recovery. The evacuation rate shall be noted.

The volume of standing water in a well will be calculated by subtracting the depth to water from the total depth of the well and then multiplying this value by a coefficient which relates the diameter of the well to gallons per linear foot. Coefficients for commonly encountered well diameters are listed on the bottom of the G & M Water Sampling Log. The volume of standing water in a well for which a coefficient is not listed can be determined by the formula:

$$V = 7.48 \pi r^2 h$$

where, V = Volume of standing water (gallons)
r = Radius of well casing (ft)
h = Height of standing water (ft)

DEC 2 1987

WATER SAMPLING LOG

ENVIRONMENT SERVICES DIVISION

Project/No. _____

Site Location _____

Site/Well No. _____

Coded/
Replicate No. _____

Date _____

Weather: _____

Time Sampling
Began _____

Time Sampling
Completed _____

EVACUATION DATA

Description of Measuring Point (MP) _____

Height of MP Above/Below Land Surface _____ MP Elevation _____

Total Sounded Depth of Well Below MP _____ Water-Level Elevation _____

Hand _____ Depth to Water Below MP _____ Diameter of Casing _____

Wet _____ Water Column in Well _____ Gallons Pumped/Bailed
Prior to Sampling _____

Gallons per Foot _____

Gallons in Well _____ Sampling Pump Intake Setting
(feet below land surface) _____

Evacuation Method _____

SAMPLING DATA/FIELD PARAMETERS

Color _____ Odor _____ Appearance _____ Temperature _____ °F/°C

Other (specific ion; OVA; HNU; etc.) _____

Specific Conductance,
umhos/cm _____ pH _____

Sampling Method and Material _____

Constituents Sampled	Container Description From Lab _____ or G&M _____	Preservative
_____	_____	_____
_____	_____	_____
_____	_____	_____

Remarks _____

Sampling Personnel _____

GAL/FT	WELL CASING VOLUMES			
	1-1/4" = 0.077	2" = 0.18	3" = 0.37	4" = 0.85
	1-1/2" = 0.10	2-1/4" = 0.24	3-1/2" = 0.50	6" = 1.48

FIGURE 3-6-2 Standard form for logging field data during

STANDARD OPERATING PROCEDURES
AND
ANALYTICAL QUALITY ASSURANCE PROGRAM
FOR
KEMRON ENVIRONMENTAL SERVICES

KEMRON QUALITY ASSURANCE MANUAL
TABLE OF CONTENTS

1.0 INTRODUCTION

- 1.1 Importance of Quality Control
- 1.2 Overview of the KEMRON Program
- 1.3 Standard Analytical Methods

2.0 SAFETY AND HOUSEKEEPING

- 2.1 General
- 2.2 Handling Chemicals
- 2.3 Hoods and Ventilation
- 2.4 Personal Protective Equipment
- 2.5 Other Safety Equipment
- 2.6 Compressed Gas Cylinders
- 2.7 Fire Protection
- 2.8 Housekeeping
- 2.9 Smoking Policy
- 2.10 Responsibility

3.0 LABORATORY SERVICES AND MATERIALS

- 3.1 General
- 3.2 Deionized Water
- 3.3 Compressed Air
- 3.4 Desiccants
- 3.5 Standard Solutions

4.0 GLASSWARE AND SAMPLE CONTAINERS

- 4.1 General
- 4.2 Selection of Glassware
- 4.3 Volumetric Glassware
- 4.4 Cleaning Requirements

5.0 SAMPLING OF WATER AND WASTEWATER

- 5.1 General
- 5.2 Sample Containers
- 5.3 Fundamentals of Sample Collection
- 5.4 Sample Preservation
- 5.5 Sample Identification
- 5.6 Chain-of-Custody Procedures
- 5.7 Field Notebook

6.0 SAMPLE HANDLING

- 6.1 General
- 6.2 Logging
- 6.3 Storage
- 6.4 Shipping

7.0 CONTROL OF ANALYTICAL PERFORMANCE

- 7.1 General Analytical Chemistry**
- 7.2 Organic Analyses**
- 7.3 Data Validation**

8.0 STANDARDS, CALIBRATION, AND INSTRUMENTATION

- 8.1 General**
- 8.2 Instrument Logs**
- 8.3 Calibration Standards**
- 8.4 Preventive Maintenance**
- 8.5 Analytical Balance**

9.0 TRAINING OF LABORATORY PERSONNEL

- 9.1 General**
- 9.2 General Orientation**
- 9.3 Safety Policy**
- 9.4 Quality Assurance Manuals**
- 9.5 Data Handling and Report**
- 9.6 Sample Logging and Handling**
- 9.7 Measuring**
- 9.8 Weighing**

10.0 LIST OF EXHIBITS

- A. Analytical Methods, References**
- B. Sample Preservation, Minimum Volumes, Maximum Holding Times**
- C. Chain-of-Custody Records**
- D. Example KEMRON Bottle Tags and Labels**
- E. QA Statistics Formula and Example Calculation**
- F. Example Pages from KEMRON Quality Assurance Notebook**
- G. Example Control Charts for Precision and Accuracy**
- H. Example Quality Assurance Reports**
 - QA Daily Report to Management/Client**
 - QA Violation Report**
- I. Calibration Standards Logbook Forms**
- J. Example KEMRON Sample Shipping Log**
- K. KEMRON Analytical Reporting Format**
 - Inorganic Analyses - Example**
- L. KEMRON Analytical Reporting Format**
 - GC/MS Analyses - Example**

1.0 INTRODUCTION

1.1 Importance of Quality Control

The laboratories which have joined together to form KEMRON Environmental Services are sharing many years of experience in environmental sampling and analysis by assembling this Quality Assurance Manual. The importance of having a sound, written quality assurance program can be best emphasized by quoting from the "Handbook for Analytical Quality Control in Water and Wastewater Laboratories":

Decisions made using water and wastewater data are far-reaching. Water quality standards are set to establish satisfactory conditions for a given water use. The laboratory data define whether that condition is being met, and whether the water can be used for its intended purpose. If the laboratory results indicate a violation of the standard, action is required on the part of pollution control authorities. With the present emphasis on legal action and social pressures to abate pollution, the analyst should be aware of his responsibility to provide laboratory results that are a reliable description of the sample. Furthermore, the analyst must be aware that his professional competence, the procedures he has used, and the reported values may be used and challenged in court.

To satisfactorily meet this challenge, the laboratory data must be backed up by an adequate program to document the proper control and application of all of the factors which affect the final results.

In wastewater analyses, the laboratory data define the treatment plant influent, the status of the steps in the treatment process, and the final load imposed upon the water resources. Decisions on process changes, plant modification, or even the construction of a new facility may be based upon the results of laboratory analyses. The financial implications alone are significant reasons for extreme care in analysis.

Research investigations in water pollution control rest upon a firm base of laboratory data. The final result sought can usually be described in numerical terms. The progress of the research and the alternative pathways available are generally evaluated on the basis of laboratory data. The value of the research effort will depend upon the validity of the laboratory results.

Because of the importance of laboratory analyses and the resulting actions which they produce, a program to insure the reliability of the data is essential. It is recognized that all analysts practice quality control to varying degrees, depending somewhat upon their training, professional pride, and awareness of the importance of the work they are doing. However, under the pressure of daily workload, analytical quality control may be easily neglected. Therefore, an established, routine control program applied to every analytical test is important in assuring the reliability of the final results.

The quality control program in the laboratory has two primary functions. First, the program should monitor the reliability (truth) of the results reported. It should continually provide an answer to "How good (true) are the results submitted?" This phase may be termed "measurement of quality." The second function is the control of quality in order to meet the program requirements for reliability... Ideally, all of the variables which can affect the final answer should be considered, evaluated, and controlled.

1.2 Overview of the KEMRON Program

By establishing a sound protocol for each field and laboratory procedure, the result is the production of valid data that addresses the client's concern in the area of accountability, traceability, documentation, security, and analytical performance.

The field sampling, laboratory processing, and data review procedures described in this manual are those used by KEMRON while conducting sampling and analysis projects. They are, however, amendable to specific client needs or special project requirements. KEMRON wishes to emphasize that our program is based soundly upon U.S. Environmental Protection Agency guidelines.

Believing that quality assurance starts long before the sampling begins and continues well past the analyses, standard operating procedures have been established in the following areas:

- .Safety and Housekeeping
- .Standard Analytical Procedures
- .Laboratory Services
- .Reagents, Solvents, Gases
- .Glassware
- .Sampling Water and Wastewater
- .Instrumentation
- .Control of Laboratory Performance
- .Data Handling and Review
- .Professional Training and Skills

1.3 Analytical Methods

KEMRON Environmental Services believes in strict adherence to accepted methods for the analysis of water and wastewater samples. Whenever possible, only recommended or approved standard analytical procedures will be used in our laboratories. For the routine analysis of water and wastewater samples required for compliance monitoring (i.e., National Pollution Discharge Elimination System permit, Safe Drinking Water Act (SDWA) and Resource Conservation and Recovery Act (RCRA)), standard analytical methods have been specified by the regulatory agencies and are closely adhered to in our laboratories.

2.0 SAFETY AND HOUSEKEEPING

2.1 General

The Occupational Safety and Health Act of 1970 covers laboratory workplaces as well as industrial and manufacturing workplaces. There is a general belief that small and medium sized laboratories can expect direct involvement with the Occupational Safety and Health Administration (OSHA) in the future. KEMRON has not waited for formal action by this agency to implement a sound safety program at each of its operations. It has been said that the value of a safety program is not measured by its affect on the "bottom-line" but on its ability to avert disaster.

2.2 Handling Chemicals

We should realize that every chemical we handle will, to some extent, represent a potential hazard or toxicity problem. Toxic materials may enter the body through the respiratory tract, digestive tract, or through the skin.

We may not be given a warning that poisoning is taking place, and we may not have sufficient time to take corrective action. If we do not know the potential hazard of a substance or unknown sample, then we must treat them with respect. Nearly all chemicals can be handled routinely and safely if we follow correct procedures. Here are some general guidelines to be followed:

1. Become familiar with the chemical and physical properties of chemicals which you handle.
2. Become familiar with their safety hazards.
3. Use correct procedures and the necessary safety equipmet. (i.e., hoods, safety glasses, goggles, respirators, gloves, etc.)
4. Use common sense and pay attention to the job you are doing.
5. Prepare for possible corrective action if by chance it is needed.

Information pertaining to chemical properties may be obtained from the following sources:

1. "Material Safety Data Sheets" - If you handle a chemical, refer to these sheets so that necessary precautions can be taken.
2. Fire Protection - "Guide on Hazardous Materials"
3. "SAC - Dangerous Properties of Industrial Materials" - Each of the laboratories should obtain a copy of this reference.
4. "Merck Index"
5. "MCA Case Histories of Accident"

General classes of hazardous chemicals are summarized below:

1. Flammable Solvents - Be familiar with a solvent's flash point and vapor density. Underwriters Laboratories has developed a standard classification for grading the relative hazard of the various flammable liquids:

Ether class	100
Gasoline class	90 - 100
Alcohol (Ethyl) class	60 - 70
Kerosene class	30 - 40
Paraffin Oil class	10 - 20

2. Strong Mineral Acids - Should be treated with respect and include hydrochloric, hydrofluoric, sulfuric, and nitric acids.
3. Oxidizing Materials - Be very careful to avoid contact of these classes with organic matter which could lead to an explosion.

Typical hazardous oxidizing agents:

Chlorine dioxide
Sodium chlorate; all chlorates
Potassium chromate
Chromium trioxide
Perchloric acid; perchlorates
Peroxides

2.3 Hoods and Ventilation

1. KEMRON laboratories will be equipped with sufficient number of hoods to adequately protect the workers from flammable, toxic or otherwise hazardous substances.
2. Make-up air should be supplied to rooms or hoods to replace the quantity of air exhausted through the hoods.
3. Hood ventilation system should be checked routinely to determine that air flow is not less than 60 ft/min (linear) across the face of the hood with all doors open and 150 ft/min (linear) of toxic materials are involved.
4. The following includes a partial list of solvents which always should be used under the hood: chloroform, carbon tetrachloride, methylene chloride and all other chlorinated hydrocarbons; benzene, toluene, pyridene, hexanes, etc.

2.4 Personal Protective Equipment

1. Laboratory coats and safety glasses are to be worn at all times within the laboratory. Each KEMRON laboratory should be clearly marked with signs, lines on floors, or other means to indicate where these items are to be worn. These areas should include the sampling logging areas, wet laboratories, sample preparation, stock rooms, all lab bench areas, bottle washing and preparation, and all instruments labs including AA and GC.
2. Respirators should be provided and used by employees when working with extremely toxic or carcinogenic substances.
3. Disposable gloves are to be provided at each laboratory to be used in handling very toxic or dangerous materials.
4. Face shields and/or goggles should be worn when the potential for explosion exists.

2.5 Other Safety Equipment

Each KEMRON facility will be equipped with a safety shower, eye wash station(s) and a first aid kit.

2.6 Compressed Gas Cylinders

2.6.1 Cylinder Receipt and Content Identification

1. When a cylinder is received from the supplier, it should have the following attached:
 - a. An identification label and/or markings indicating the contents.
 - b. An I.C.C. label
 - c. A valve protection cap
2. Do not remove any of the labels. The valve protection cap must not be removed until the cylinder is properly anchored in place and ready for use.

2.6.2 Storage

1. Cylinders must be stored away from heat, be protected from direct sunlight and placed in a dry, well-ventilated area. Subsurface storage locations are to be avoided.

2. Cylinders must always be chained in place to prevent them from falling.
3. Unauthorized personnel must never tamper with a cylinder.
4. Do not store FULL and EMPTY cylinders together. Serious suckback can occur when an empty cylinder is attached to a pressurized system.
5. When a cylinder is considered empty, the valves must be closed, and all protective caps and other accessories shipped with the cylinder attached to it. The cylinder must then be labeled "EMPTY" or "MT" and placed in the proper storage area, away from full cylinders.

2.6.3 Handling

1. Never drop cylinders, or let them strike against each other violently.
2. *Do not drag, roll, or slide cylinders. Cylinders must be moved by a special cart provided for this (except lecture bottles and size #4 cylinders which are small enough to be carried).
3. Never tamper with safety devices in cylinders or valves.
4. No part of a cylinder should be subjected to a temperature higher than 125° F. Never permit flame to come in contact with a cylinder.
5. Do not use a cylinder where it may become a part of an electric current.
6. Cylinders must be clamped or chained securely to prevent them from falling over. Be sure the chain is located high enough on the cylinder so it cannot possibly tumble out.
7. Use piping and fittings, suitable for the contained gas and pressure, installed in accordance with accepted methods. Provide cylinder valves, regulators and safety relief devices, and use only approved manifolds for connecting cylinders together.

* An exception to the rule is when transferring cylinders in field (remote) installations.

8. Provide ventilation for indoor cylinder areas. Natural ventilation will usually be adequate for lighter-than-air-gases.
9. Do not attempt to repair a leak between regulator and cylinder with the cylinder valve open.
10. Never use oil on or around an oxygen regulator. Use only water-pumped, not oil-pumped, gas equipment with oxygen cylinders. (Oil, with oxygen under pressure, will explode).
11. Never use Carbon Tetrachloride to clean out oxygen lines.
12. Know the flammability, toxicity, etc., of the gases you will be handling. Familiarize yourself with the first aid methods to be employed in cases of overexposure or burns caused by a gas. Know where safety equipment such as gas masks, safety shower, etc., are located.

2.7 Fire Protection

- 2.7.1 Fire extinguisher (CO₂ type) are to be provided at conventional locations, and personnel should be instructed in their use.
- 2.7.2 Laboratory personnel will be adequately trained regarding pertinent fire hazards.

2.8 Housekeeping

Housekeeping plays an important role in the reduction of the frequency of laboratory accidents. Rooms will be kept in a neat and orderly condition. Floors, shelves, tables and lab benches will be kept free from dirt and from all apparatus and chemicals not in use. A cluttered laboratory is a dangerous place to work and tends to encourage "sloppy" laboratory technique and habits. Specific guidelines for all KEMRON laboratories to follow shall include the following:

1. Passageways shall be kept clear to all building exits and stairways.
2. Laboratories shall be swept daily to keep the floors clear of all dirt and litter.
3. Chemical spills shall be cleaned up immediately.
4. Laboratory benches and hoods shall be sponged on a daily basis or after each use whichever is needed.
5. Laboratories shall be mopped at least twice per month.
6. Laboratory instruments shall be wiped with a damp cloth at least weekly to keep them free of dirt and chemicals. Balances will need daily care to keep them clean.
7. Containers will be provided at each laboratory for the disposal of broken glassware and shall be properly labeled.
8. Separate approved waste disposal cans shall be provided for disposal of waste solvents.
9. Flammable liquids, liquids not miscible with water, and corrosive materials or compounds that are likely to give off toxic compounds shall never be poured into the sinks.

2.9 Smoking Policy

Smoking shall not be permitted by any employee in laboratory, storage rooms, and instrument rooms of the KEMRON facilities. Smoking shall be restricted to office and lunchroom areas.

2.10 Responsibility

Responsibility for implementation of the safety and housekeeping procedures of this manual shall be assigned to Regional Managers. Laboratory supervisors and program managers shall be responsible for enforcement of the safety and housekeeping rules. Responsibility for specific housekeeping tasks shall be delegated to individual staff members.

3.0 LABORATORY SERVICES AND MATERIALS

3.1 General

Quality control of the wastewater and other environmental/ analytical laboratory analyses involves consideration and control of many variables that affect the production of reliable data. The most skilled technician working with the most sophisticated of modern instrumentation cannot produce quality data, if the quality of basic laboratory reagents, solvents, and other services are not controlled. Therefore, it is essential that the laboratory have an abundant supply of interference free distilled or deionized water, an adequate supply of clean compressed air, and use the best available reagents, solvents, and specialty gases.

3.2 Deionized Water

3.2.1 System Description

High purity water at each KEMRON facility is produced by commercially manufactured systems using ion exchange, carbon absorption, and membrane filtration. The typical system consists of a series of tanks beginning with carbon absorption, cation exchange, anion exchange, two or more mixed bed ion exchange tanks, followed by carbon absorption and 0.45 μm filtration. This system is capable of producing water with a maximum total matter content of 0.1 mg/l and a maximum conductivity of 1.0 $\mu\text{mho/cm}$ at 25°C, which meets the ASTM specification for Type II Reagent water.

The addition of a 0.2 μm membrane filter at the end of the deionizing system is required to produce ASTM Type I grade of water.

3.2.2 Quality Control Checks

1. Conductivity checks on the system are to be performed daily. If the system is not equipped with its own monitoring lights (or meters), the conductivity must be determined using a laboratory meter and a cell with a constant of 0.1 cm^{-1} . Systems which rely on built-in meters or lights should contain those devices after both the first and second mixed bed ion-exchange tanks. The vendor should be called for services when the first light goes out, or any time the conductivity exceeds 1 $\mu\text{mho/cm}$ at 25°C.
2. pH determinations are required daily. pH values will normally fall between 4 and 10.

3. TOC measurements are required weekly. TOC should not exceed 1 mg/LC for general use.
4. Total residual chlorine tests should be performed weekly. Any detectable chlorine, using the HACH DPD method or equivalent, is unacceptable and must be corrected.
5. A record of conductivity, pH, chlorine residual, and TOC are to be maintained in a bound logbook. Entries should include the test names, results, initials of analyst, and control limits. The record book should also have space for comments and records of service. The usage rate can also be tracked with those systems equipped with meters (gallons).

3.3 Compressed Air

Zero grade air for such instrumentation as AA and TOC may be purchased in large capacity cylinders or generated by a compressor system. In the latter case, it is necessary that the air produced be purified by a system of filters to remove oil mist, particulates, desiccants for moisture removal, and special scrubbers in some applications.

3.4 Desiccants

Desiccators are used to dry reagents used for volumetric standards and to dry apparatus and containers involved in gravimetric determination. To assure that the desiccator performs efficiently, it is necessary that the desiccant be properly maintained.

1. The desiccant should be of the indicating silica gel type and changed whenever the color changes from blue to pink.
2. The desiccant should be checked daily and replaced at least once per week, or as needed under humid conditions.

3.5 Standard Solutions

3.5.1 General

Chemical reagents are available in a wide variety of grades and purity, and the factors determining the grade selected are the parameter of interest and the sensitivity of the detection system.

Primary standards and calibration standards should be traceable to a Standard Reference Material (SRM) produced by the National Bureau of Standards (NBS) if at all possible.

Not all analytical parameters have primary grade or NBS traceable standards available. In this situation, the highest quality reagent of known purity should be used, and the concentration of the stock corrected for purity.

3.5.2 Primary Standards

The highest quality analytical standards are the Standard Reference Materials available from the National Bureau of Standards. Primary standard grade reagents are available from scientific companies, and may be used, if traceability to NBS standards is documented. The following primary standards are to be maintained in each KEMRON laboratory.

1. Buffers
 - a. Potassium Hydrogen Phthalate (KHP)
 - b. Borax
 - c. Potassium Dihydrogen Phosphate (KH_2PO_4)
Disodium Hydrogen Phosphate (Na_2HPO_4)
2. Acidimetric/Alkalimetric Standards
 - a. Sodium Carbonate
 - b. KHP
3. Redox Standards
 - a. Potassium Dichromate
 - b. Potassium Bromate (for Phenolics analyses only)

3.5.3 Storing and Maintaining Reagents and Solvents

1. The analytical method should be consulted for the proper storage container for each reagent. Plastic containers are acceptable for most inorganic determinations, but borosilicate glass should be used for reagents intended for organic analyses.
2. The analytical method will specify a reagent's shelf life. All reagents should be dated and the solution either discarded or restandardized when the expiration dates have been exceeded.
- 3. Each reagent must be labeled with the following information:
 - a. Name of reagent
 - b. Concentration with units
 - c. Initials of preparer
 - d. Preparation date
 - e. Expiration date
4. Records for the preparation and standardization of primary standards and volumetric standards must be maintained in bound chemist notebooks, and periodically reviewed by the lab supervisor.

Additional details on the preparation of concentrated stock standards and working standards for instrument calibration are given in Section 8.3. Exhibit I gives examples from the KEMRON Standards Logbook.

3.5.4 General Inorganic Analyses

For inorganic analyses, AR grade reagents and solvents are satisfactory and generally may be used. Primary standards must be used to standardize the volumetric solutions, but commercially available reagents are used after it has been demonstrated that they meet method requirements. Compressed air used for the total organic carbon analyzer should be Zero Grade.

1. Reagent blanks must be analyzed in every batch of analyses.
2. Calibration curves must be verified after any change in reagents. Analysis of a blank and at least three standards is sufficient to determine if a new curve is required.

3.5.5 Metals Analyses

1. All reagents used for the preparation of atomic absorption standards should be spectroquality.
2. Commercial atomic absorption standards may also be used in KEMRON laboratories, but must always be traced to previous standards and expiration dates must be carefully monitored. Stocks must be prepared or purchased at least yearly, regardless of the specified expiration date or recommended shelf lives.
3. Nitric and hydrochloric acids must be of a grade specified for trace metal analyses.
4. The determination for mercury requires special grade reagents specifically produced for this determination. Nitric acid, sulfuric acid, potassium permanganate, potassium persulfate, hydroxylamine, and stannous sulfate should all specify "for the analysis of mercury".
5. Reagent blanks must be analyzed in every batch of analyses.

3.5.6 Organic Chemical Analyses

1. The purity of reagents that may be used for organic analyses is AR grade or better.
2. Reference grade standards should be used when available from NBS or EPA.
3. Solvents used in analysis of pesticides and PCBs by GC/ECD should be "Pesticide Grade" or the equivalent.
4. Specialty gases for GC analyses should be of the highest quality available, unless it can be demonstrated that a lower grade is acceptable.
5. Argon-methane used for the electron-capture-detector must have an oxygen trap and a molecular sieve drying tube. These should be changed or regenerated with each new cylinder of carrier gas.
6. The nitrogen detector requires the use of ultra-pure hydrogen for satisfactory results.
7. All cylinder gases must be replaced when the pressure falls to the 100 to 200 psi range.
8. A method blank is required with every batch of analyses to assure that all reagents, solvents and gases are interference free.
9. If problems are encountered in the method blank, then individual reagent blanks must be analyzed to determine the problem reagent.

REFERENCES

- (1) "Methods for Chemical Analysis of Water and Wastes," U.S. Environmental Protection Agency, EPA-600/4-79-020, revised March, 1983.
- (2) "Manual of Analytical Methods for the Analysis of Pesticides in Humans and Environmental Samples," U.S. Environmental Protection Agency, EPA-600/8-8-038, June, 1980.
- (3) EPA-600/4-80-032, U.S. Environmental Protection Agency, 1980.
- (4) "Standard Methods for the Examination of Water and Wastewater," APHA-AWWA-WPCF, 15th Edition, 1980.
- (5) "Total Organic Halide," U.S. Environmental Protection Agency, Method 450.1 Interim, November, 1980.
- (6) "Standard Methods for the Examination of Water and Wastewater," APHA-AWWA-WPCF, 14th Edition, 1975.
- (7) "Test Methods for the Evaluation of Solid Waste," U.S. Environmental Protection Agency, Physical/Chemical Methods (SW-846).
- (8) "Annual Book of ASTM Standards," The American Society for Testing and Materials, 1980.
- (9) "Annual Book of ASTM Standards," The American Society for Testing and Materials, Part 31, 1981.
- (10) Hach COD System, Hach Chemical Company (See Federal Register, April 21, 1980, page 26811).
- (11) "NIOSH Manual of Analytical Methods," U.S. Department of Health, Education, and Welfare, Volume 1, Second Edition.
- (12) EPA 600/4-80-032 1980.
- (13) "Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater," U.S. Environmental Protection Agency, EPA-600/4-82-057, July, 1982.

EXHIBIT B

Sample Preservation

Minimum Volumes

Maximum Holding Times

SAMPLE PRESERVATION

Complete and unequivocal preservation of samples, either domestic sewage, industrial wastes, or natural waters, is a practical impossibility. Regardless of the nature of the sample, complete stability for every constituent can never be achieved. At best, preservation techniques can only retard the chemical and biological changes that inevitably continue after the sample is removed from the parent source. The changes that take place in a sample are either chemical or biological. In the former case, certain changes occur in the chemical structure of the constituents that are a function of physical conditions. Metal cations may precipitate as hydroxides or form complexes with other constituents; cations or anions may change valence states under certain reducing or oxidizing conditions; other constituents may dissolve or volatilize with the passage of time. Metal cations may also adsorb onto surfaces (glass, plastic, quartz, etc.), such as, iron and lead. Biological changes taking place in a sample may change the valence of an element or a radical to a different valence. Soluble constituents may be converted to organically bound materials in cell structures, or cell lysis may result in release of cellular material into solution. The well known nitrogen and phosphorus cycles are examples of biological influence on sample composition. Therefore, as a general rule, it is best to analyze the samples as soon as possible after collection. This is especially true when the analyte concentration is expected to be in the low $\mu\text{g/l}$ range.

Methods of preservation are relatively limited and are intended generally to (1) retard biological action, (2) retard hydrolysis of chemical compounds and complexes, (3) reduce volatility of constituents, and (4) reduce absorption effects. Preservation methods are generally limited to pH control, chemical addition, refrigeration, and freezing.

The recommended preservative for various constituents is given in Table 1. These choices are based on the accompanying references and on information supplied by various Quality Assurance Coordinators. As more data become available, these recommended holding times will be adjusted to reflect new information. Other information provided in the table is an estimation of the volume of sample required for the analysis, the suggested type of container, and the maximum recommended holding times for samples properly preserved.

TABLE 1

RECOMMENDATION FOR SAMPLING AND PRESERVATION
OF SAMPLES ACCORDING TO MEASUREMENT⁽¹⁾

<u>Measurement</u>	<u>Vol. Req. (ml)</u>	<u>Container</u> ²	<u>Preservative</u> ^{3,4}	<u>Holding Time</u> ⁵
100 <u>Physical Properties</u>				
Color	50	P,G	Cool, 4°C	48 Hrs.
Conductance	100	P,G	Cool, 4°C	28 Days
Hardness	100	P,G	HNO ₃ to pH < 2	6 Mos.
Odor	200	G only	Cool, 4°C	24 Hrs.
pH	25	P,G	None Req.	Analyze Immediately
Residue				
Filterable	100	P,G	Cool, 4°C	7 Days
Non- Filterable	100	P,G	Cool, 4°C	7 Days
Total	100	P,G	Cool, 4°C	7 Days
Volatile	100	P,G	Cool, 4°C	7 Days
Settleable Matter	1000	P,G	Cool, 4°C	48 Hrs.
Temperature	1000	P,G	None Req.	Analyze Immediately
Turbidity	100	P,G	Cool, 4°C	48 Hrs.
200 <u>Metals</u>				
Dissolved	200	P,G	Filter on site HNO ₃ to pH < 2	6 Mos.
Suspended	200		Filter on site	6 Mos. ⁽⁸⁾
Total	100	P,G	HNO ₃ to pH < 2	6 Mos.

TABLE 1 (CONT)

<u>Measurement</u>	<u>Vol. Req. (ml)</u>	<u>Container²</u>	<u>Preservative^{3,4}</u>	<u>Holding Time⁵</u>
Chromium ^{*8}	200	P,G	Cool, 4°C	24 Hrs.
Mercury Dissolved	100	P,G	Filter HNO ₃ to pH < 2	28 Days
Total	100	P,G	HNO ₃ to pH < 2	28 Days
300 <u>Inorganics, Non-Metallics</u>				
Acidity	100	P,G	Cool, 4°C	14 Days
Alkalinity	100	P,G	Cool, 4°C	14 Days
Bromide	100	P,G	None Req.	28 Days
Chloride	50	P,G	None Req.	28 Days
Chlorine	200	P,G	None Req.	Analyze Immediately
Cyanides	500	P,G	Cool, 4°C NaOH to pH > 12 0.6g ascorbic acid ⁶	14 Days ⁷
Fluoride	300	P,G	None Req.	28 Days
Iodide	100	P,G	Cool, 4°C	24 Hrs.
Nitrogen				
Ammonia	400	P,G	Cool, 4°C H ₂ SO ₄ to pH < 2	28 Days
Kjeldahl, Total	500	P,G	Cool, 4°C H ₂ SO ₄ to pH < 2	28 Days
Nitrate plus Nitrite	100	P,G	Cool, 4°C H ₂ SO ₄ to pH < 2	28 Days
Nitrate ⁹	100	P,G	Cool, 4°C	48 Hrs.
Nitrite	50	P,G	Cool, 4°C	48 Hrs.

TABLE 1 (CONT)

<u>Measurement</u>	<u>Vol. Req. (ml)</u>	<u>Container²</u>	<u>Preservative^{3,4}</u>	<u>Holding Time⁵</u>
Dissolved Oxygen Probe	300	G bottle and top	None Req.	Analyze Immediately
Winkler	300	G bottle and top	Fix on site and store in dark	8 Hours
Phosphorus Ortho- phosphate, Dissolved	50	P,G	Filter on site Cool, 4°C	48 Hrs.
Hydrolyzable	50	P,G	Cool, 4°C H ₂ SO ₄ to pH < 2	28 Days
Total	50	P,G	Cool, 4°C H ₂ SO ₄ to pH < 2	28 Days
Total, Dissolved	50	P,G	Filter on site Cool, 4°C H ₂ SO ₄ to pH < 2	24 Hrs.
Silica	50	P only	Cool, 4°C	28 Days
Sulfate	50	P,G	Cool, 4°C	28 Days
Sulfide	500	P,G	Cool, 4°C add 2 ml zinc acetate plus NaOH to pH > 9	7 Days
Sulfite	50	P,G	None Req.	Analyze Immediately
400 <u>Organics</u>				
BOD	1000	P,G	Cool, 4°C	48 Hrs.
COD	50	P,G	Cool, 4°C H ₂ SO ₄ to pH < 2	28 Days
Oil & Grease	1000	G only	Cool, 4°C H ₂ SO ₄ to pH < 2	28 Days
Organic carbon	25	P,G	Cool, 4°C H ₂ SO ₄ or HCl to pH < 2	28 Days
Phenolics	500	G only	Cool, 4°C H ₂ SO ₄ to pH < 2	28 Days

TABLE 1 (CONT)

<u>Measurement</u>	<u>Vol. Req. (ml)</u>	<u>Container²</u>	<u>Preservative^{3,4}</u>	<u>Holding Time⁵</u>
MBAS	250	P,G	Cool, 4°C	48 Hrs.
NTA	50	P,G	Cool, 4°C	24 Hrs.

1. More specific instructions for preservation and sampling are found with each procedure as detailed in this manual. A general discussion on sampling water and industrial wastewater may be found in ASTM, Part 31, p. 72-82 (1976) Method D-3370.
2. Plastic (P) or Glass (G). For metals, polyethylene with a polypropylene cap (no liner) is preferred.
3. Sample preservation should be performed immediately upon sample collection. For composite samples each aliquot should be preserved at the time of collection. When use of an automated sampler makes it impossible to preserve each aliquot, then samples may be preserved by maintaining at 4°C until compositing and sample splitting is completed.
4. When any sample is to be shipped by common carrier or sent through the United States Mails, it must comply with the Department of Transportation Hazardous Materials Regulations (49 CFR Part 172). The person offering such material for transportation is responsible for ensuring such compliance. For the preservation requirements of Table 1, the Office of Hazardous Materials, Materials Transportation Bureau, Department of Transportation has determined that the Hazardous Materials Regulations do not apply to the following materials: Hydrochloric acid (HCl) in water solutions at concentrations of 0.04% by weight or less (pH about 1.96 or greater); Nitric acid (HNO₃) in water solutions at concentrations of 0.15% by weight or less (pH about 1.62 or greater); Sulfuric acid (H₂SO₄) in water solutions at concentrations of 0.35% by weight or less (pH about 1.15 or greater); Sodium hydroxide (NaOH) in water solutions at concentrations of 0.080% by weight or less (pH about 12.30 or less).
5. Samples should be analyzed as soon as possible after collection. The times listed are the maximum times that samples may be held before analysis and still considered valid. Samples may be held for longer periods only if the permittee, or monitoring laboratory, has data on file to show that the specific types of sample under study are stable for the longer time, and has received a variance from the Regional Administrator. Some samples may not be stable for the maximum time period given in the table. A permittee, or monitoring laboratory, is obligated to hold the sample for a shorter time if knowledge exists to show this is necessary to maintain sample stability.
6. Should only be used in the presence of residual chlorine.

7. Maximum holding time is 24 hours when sulfide is present. Optionally, all samples may be tested with lead acetate paper before the pH adjustment in order to determine if sulfide is present. If sulfide is present, it can be removed by the addition of cadmium nitrate powder until a negative spot test is obtained. The sample is filtered and then NaOH is added to pH 12.
8. Samples should be filtered immediately on-site before adding preservative for dissolved metals.
9. For samples from non-chlorinated drinking water supplies conc. H_2SO_4 should be added to lower sample pH to less than 2. The sample should be analyzed before 14 days.

EXHIBIT C

Chain-of-Custody Records

KEMRON Environmental Services
901 Highland Avenue
Williamstown, WV 26187
(304)375-5800

CHAIN OF CUSTODY RECORD

[illegible]

EXHIBIT D

KEMRON Bottle Tags and Labels

KEMRON SAMPLE TAG

Client—STANDARD OIL CO. AND SUBSIDIARIES

Location: _____ Outfall _____

Date: _____ Time: _____ Flowrate (gpm) _____

Water Temp. (°C or °F) _____ Preservative Added Yes ☐ No ☐

Analyses: To be performed (check):

Oil and Grease ☐ Dissolved Iron ☐ pH ☐

TSS ☐ Petro. Hydro. ☐ Other _____

On site pH result _____

Sample by: _____
(please print name)

KEMRON®

CLIENT _____

SAMPLE SOURCE _____

DATE _____ TIME _____

PARAMETER(S) _____

PRESERVATIVE _____



Kemron Environmental Services

- ☐ BATON ROUGE, LOUISIANA, 16550 HIGHLAND ROAD, (504) 293-8650 ZIP 70808 •
- ☐ CHICAGO, ILLINOIS, 3570 NORTH AVONDALE AVENUE, (312) 588-8500 ZIP 60618 •
- ☐ FARMINGTON HILLS, MICHIGAN, 32740 NORTHWESTERN HIGHWAY, (313) 626-2426 ZIP 48018 •
- ☐ MARIETTA, OHIO, 235 SECOND STREET, (614) 374-2222 ZIP 45750 •
- ☐ PORT NECHES, TEXAS, 1216 PORT NECHES AVENUE, (713) 727-1661 ZIP 77651

Analysis Requisition for _____

Date _____ Time _____

Sample Source _____

Analysis Requisitioned _____

Report results as _____

(e.g. ppm, dry basis, etc.)

EPA Method _____ Other _____

Hazardous or Toxic Substances _____

Comments _____

Report To: _____

No. Copies _____ P.O. No. _____

Results Required (Date) _____

Kemron Log No. _____

EXHIBIT E

QA Statistics Formula and Calculations

(1) The Accuracy Control Chart: \bar{X} Chart

\bar{X} , the actual value of the standard as prepared, will be used together with the upper and lower accuracy control limit to construct the accuracy control chart. $UCL_{\bar{X}}$, $LCL_{\bar{X}}$, which are upper and lower accuracy control limits for 95% confidence limit, respectively, calculated as:

$$UCL_{\bar{X}} = \bar{X} + 2 \sigma_{\bar{X}}$$

$$LCL_{\bar{X}} = \bar{X} - 2 \sigma_{\bar{X}}$$

where $\sigma_{\bar{X}}$ = standard deviation, calculated as

$$\sigma_{\bar{X}} = \sqrt{\frac{\sum_{i=1}^n (\bar{x}_i - \bar{x}_c)^2}{n}}$$

\bar{x}_i : observed average value for each set of duplicated standards

$$\bar{x}_c = \frac{\sum_{i=1}^n \bar{x}_i}{n}$$

(2) The Precision Control Chart: R Chart

\bar{R} , the average range, will be used together with upper and lower precision control limits to construct the precision control chart. UCL_R , LCL_R which are upper and lower precision control limits for 95% confidence limit, respectively, calculated as:

$$UCL_R = \bar{R} + 2 \sigma_R$$

$$LCL_R = \bar{R} - 2 \sigma_R$$

where $\sigma_R = \sqrt{\frac{\sum_{i=1}^n (R_i - \bar{R})^2}{n}}$, $\bar{R} = \frac{\sum_{i=1}^n R_i}{n}$

TABLE I (Cont.)
QUALITY ASSURANCE NOTEBOOKS

X CHART

$$\bar{X}_c = 121 + 118 + 115 + 131 + 126 + 125 + 121 + 131 + 135 + 131 + 131 + \dots + 124 + 125/20 = 126$$

$$c_{\bar{X}} = \sqrt{(126-121)^2 + (126-118)^2 + (126-115)^2 + \dots + (126-124)^2 + (126-125)^2/20} = 5$$

For \bar{X} chart 95% confidence limit

(accuracy chart)

$$\bar{X} = 121$$

$$UCL_{\bar{X}} = \bar{X} + 2 c_{\bar{X}} = 121 + 2 \times 5 = 131$$

$$LCL_{\bar{X}} = \bar{X} - 2 c_{\bar{X}} = 121 - 2 \times 5 = 111$$

Calculation: 1

R CHART

$$\bar{R} = 5 + 4 + 3 + 0 + 4 + \dots + 10 + 6/20 = 4.5$$

$$c_R = \sqrt{(5-4.5)^2 + (4-4.5)^2 + (3-4.5)^2 + (0-4.5)^2 + \dots + (10-4.5)^2 + (6-4.5)^2/20} = 3.1$$

For R chart, 95% confidence limit

(precision chart)

$$\bar{R} = 4.5$$

$$UCL_R = \bar{R} + 2 c_R = 4.5 + 3.1 \times 2 = 10.7$$

$$LCL_R = \bar{R} - 2 c_R = 4.5 - 3.1 \times 2 = 0$$

Calculation: 1

EXHIBIT F

**Example Pages from
KEMRON Quality Assurance Notebook**

TABLE I
QUALITY ASSURANCE NOTEBOOKS

Sample Identification: TOC and Date	Quality Assurance Reference Standards		Range (Ri)	Average Found	Set-Up By	Analyzed By	Comments
	Actual (\bar{X})	Actual Found					
4/1	121	118	5	121			
	121	123					
4/2	121	116	4	118			
	121	120					
4/3	121	116	3	115			
	121	113					
4/4	121	131	0	131			
	121	131					
4/5	121	124	4	126			
	121	128					
4/6	121	119	12	125			
	121	131					
4/7	121	120	2	121			
	121	122					
4/8	121	128	6	131			
	121	134					

TABLE I (Cont.)
QUALITY ASSURANCE NOTEBOOKS

Sample Identification: TOC and Date	Quality Assurance Reference Standards		Range (Ri)	Average Found	Set-Up By	Analyzed By	Comments
	Actual (\bar{X})	Actual Found					
4/9	121	136	3	135			
	121	133					
4/10	121	133	4	131			
	121	129					
4/11	121	129	4	131			
	121	133					
4/12	121	124	4	122			
	121	120					
4/13	121	124	8	128			
	121	132					
4/14	121	128	2	127			
	121	126					
4/15	121	130	8	134			
	121	138					
4/16	121	122	0	122			
		122					

TABLE I (Cont.)
QUALITY ASSURANCE NOTEBOOKS

Sample Identification: TOC and Date	Quality Assurance Reference Standards		Range (Ri)	Average Found	Set-Up By	Analyzed By	Comments
	Actual (\bar{X})	Actual Found					
4/17	121	119	4	121			
	121	123					
4/18	121	126	1	127			
	121	127					
4/19	121	129	10	124			
	121	119					
4/20	121	122	6	125			
	121	128					
4/21	121	124	4	122			
	121	120					
4/22	121	128	8	124			
	121	120					
4/23	121	130	14	123			Exceeds R Chart Upper
	121	116					Control Limit.
4/24	121	112	6	109			Exceeds \bar{X} Chart Lower
	121	106					Control Limit.

4.0 GLASSWARE AND SAMPLE CONTAINERS

4.1 General

The measurement of trace constituents in water demands methods capable of maximum precision and sensitivity. The selection and proper care of laboratory glassware and sample containers play an important role in quality control program, since the very sensitive analytical systems are subject to errors from improper choice of apparatus, as well as the contamination affects due to improper cleaning procedures.

4.2 Selection of Glassware

Laboratory vessels serve three functions: storage of reagents and samples, measurement of solution volumes, and confinement of reactions. Listed below are some guidelines for the proper selection of laboratory glassware:

1. Borosilicate glass, i.e., "Pyrex" or "Kimax," should be the mainstay of the laboratory. Other special types of glass are generally not required for the analyses given in "Methods for Chemical Analysis of Water and Wastes".
2. "Soft glass" should not be used.
3. The analytical method usually states when borosilicate type glassware is not acceptable. A notable example is the analysis of boron, where the reactions are carried out in platinum or Teflon vessels.
4. Unless otherwise stated, borosilicate glass or polyethylene bottles are acceptable for storage of reagents used in inorganic analyses.
5. Storage of standards used in atomic absorption analyses should be in polyethylene container, except where noted in the method, i.e., silver.
6. Storage of reagents and standards used in trace organic analyses (IR, GC, LC, GC/MS) should be in borosilicate glass only.

4.3 Volumetric Glassware

The precision of volumetric work depends in part on the precision with which volumes of samples and other reagents can be measured. By common usage, accurately calibrated glassware for precise measurement of volume has become known as volumetric glassware. Glassware that meets Federal Specification for Volumetric Glassware is designated as Class A. Except for NBS certified glassware, Class A is the most precise grade and is available in burets, volumetric flasks, and volumetric pipets. Class A glassware must be used in the following laboratory procedures:

1. Preparation of all primary standards require Class A volumetric flasks.
2. Preparation and dilution of stock standards require Class A flasks and Class A pipets.
3. All standardizations require the use of Class A burets, volumetric flasks, and pipets.
4. Class A glassware should be used at all times it is specified in the standard analytical method.

4.4 Cleaning Requirements

4.4.1 General

The following general cleaning procedures are to be used for all laboratory glassware and reusable sample bottles (glass).

All glassware should be rinsed with tap water as soon as possible after use by the analyst. In those cases where chromic acid is required, it should be used at this stage of the cleaning procedure.

Glassware to be washed should be placed in plastic trays on portable carts and returned to the wash area. The following washing procedure is given all glassware and sample bottles:

1. Soaked in hot water containing a liquid laboratory detergent such as Liquenox. Dirty vessels may require brushing.
2. Tap water rinse. At least five rinses to remove all traces of detergent.
3. Three rinses with deionized water.
4. Air dried or rinsed with AR grade acetone.

4.4.2 Special Requirements for Trace Metals Glassware

The general washing procedure is followed by the following additional procedures:

1. Rinsed with hot 1:1 nitric acid or rinsed with a mixture of nitric and hydrochloric acids (mercury analysis).
2. Rinsed with deionized water.

(Note: Glassware used for atomic absorption should be so marked and restricted for this application.)

4.4.3 Phosphate Analyses

Glassware used for phosphate or total phosphorus determination should be rinsed with hot 1:1 HCl and dedicated to this use.

4.4.4 Special Requirement for Trace Organic Analyses

In addition to the general washing procedures listed in 4.4, the following procedures should be employed in GC, LC, GC/MS and other trace organic analyses:

1. Chromic acid soaks (15 min.) are strongly recommended in several EPA publications. As a minimum, they should be used on all glassware known to have contained standards or glassware that resists cleaning attempts by other procedures.
2. Tap water rinses to remove all traces of the chromic acid.
3. Hot detergent wash
4. Tap water rinse. At least five times.
5. Deionized water rinse. Three times.
6. Air dried on dowel rack or acetone rinse to remove water.
7. Final rinse with pesticide grade hexane. (Caution: extremely flammable.) The use of methylene chloride as final rinse should be avoided due to potential contamination of VOA sample vials.

5.0 SAMPLING OF WATER AND WASTEWATER

5.1 General

The quality of data obtained from water and wastewater survey is dependent upon the following types of activities: formulation of the sampling objectives of a particular project, maintaining the integrity of samples by proper handling and preservation, proper identification of samples and adequate chain-of-custody procedures, field quality assurance, and proper field analytical procedures.

5.2 Sample Containers

A very important phase of any sampling project is the proper selection and preparation of the sample bottles at the laboratory. Exhibit B gives details of the type of containers that the EPA recommends for a particular parameter. This table also lists the preservative and holding time requirements. The washing procedures for sample bottles should be identical to those given for glassware in Section 4.4. Particular attention must be given to the special requirements for sample bottles for trace metals, mercury, phosphorus species, oil and grease and trace organics analyses. The following table summarizes the EPA recommended container type and washing procedures for the usual parameter classes.

<u>Parameter or Group</u>	<u>Container Type</u>	<u>Preparation Procedures</u>
General inorganics	1 or 2	A
Trace metals	1 or 2	A, B
Phosphorus species	1 or 2	A, C
Trace organics, extractable priority pollutants (PP), GC, GC/MS	3	A, D, E, F
Oil and grease	2, 3	A, D
Volatile Priority Pollutants (VOA vials)	4	A, G
Bacteriological	5	A, H

A. General washing procedure consisting of soaking in hot detergent, followed by 5 tap water rinses and at least 5 deionized water rinses.

B. Rinse with 1:1 nitric acid

- C. Rinse with hot 1:1 hydrochloric acid
- D. Rinse with acetone (AR grade)
- E. Rinse with hexane (Pesticide grade)
- F. Preliminary treatment with chromic acid
- G. Dried in oven
- H. Autoclaved for 15 min. each

Container Type

- 1. Polyethylene cube or bottle with polyethylene caps - one liter size
- 2. Glass bottle, clear or amber, wide mouth or Boston Round, with polyethylene lined caps - one liter size
- 3. Borosilicate glass bottles with Teflon lined caps
- 4. 40 ml borosilicate glass vials with Teflon faced silicone septa
- 5. 250 ml amber glass bottle with autoclavable caps (Bakelite)

5.3 Fundamentals of Sample Collection

5.3.1 General

The objectives of a specific sampling are usually pre-determined by the client and are formulated as the result of planning, permitting, compliance, enforcement, design, process control, and research and development.

The collection of representative samples involves the following factors: site selection, sample type, manual or automatic samplers, and flow measurements.

5.3.2 Collecting Grab Samples

- A. Grab samples may be taken at effluent points or from standing bodies of water.
- B. As a general rule it is not a good idea to rinse the sample container with sample before filling. In many cases a preservative is added to sample bottle at the laboratory.

C. Sample bottles should be filled to about 95% of capacity except for these important exceptions:

1. pH samples should be filled completely full with no headspace.
2. Samples for volatile organic analyses (VOA) are collected in special vials with Teflon faced silicone septa. These samples should be collected with no bubbles or headspace by filling the vial to capacity and carefully adding the last few ml so that a convex surface forms on the sample. The septum is then carefully placed on the vial so that no headspace forms. (Bubbles may form later due to changes in solubility of the gases and this is unavoidable.)
3. TOX samples should be collected with no bubbles or headspace.

5.3.3 Composite Samples

Manual Composite samples may be collected by taking grab samples at regular time intervals and then combining the grabs at the end of sampling interval.

KEMRON usually will use automatic samplers when collecting composite samples, since all of our laboratories are equipped with ISCO Model Automatic Samplers.

Special notes on the use of auto samplers:

- A. All tubing and the sample collection vessel should be thoroughly cleaned in a manner appropriate for the parameters of interest.
- B. Tygon tubing is acceptable for many samples but Teflontubing must be used when samples are to be analyzed for the organic priority pollutants or other analyses for GC/MS or GC/ECD. Furthermore, the 5 gal polyethylene containers in the ISCO samplers must be replaced with glass containers for the same reasons.

5.4 Sample Preservation

Use of cooling, pH control, and chemicals to retard biological activity or to stabilize the chemical species in a water sample is known as preservation. The most common form of preservation is cooling the samples to 4° C by either using ice or refrigeration.

The following is a list of the common laboratory reagents used as a preservative, and all field and laboratory personnel should be thoroughly trained in their use:

- A. Hydrochloric Acid, ACS Grade, dilute 1:1 with deionized water

- B. Nitric Acid, Baker ACS Grade for trace metal analyses, dilute 1:1
- C. Sulfuric Acid, ACS Grade, dilute 1:4
- D. Sodium Hydroxide, ACS Grade, 50% solution
- E. Sodium Thiosulfate, ACS Grade solution (for de-chlorination)

Notes on the use of preservatives

- A. The most convenient and safe procedure for preservation involves the use of individually packaged ampoules.
- B. If ampoules are not available, automatic dispensing pipettes of all glass and Teflon construction should be used in the field kits.
- C. Generally 3 ml per liter of sample is sufficient quantity to lower the pH to <2 (>12 in the case of cyanide samples preserved with NaOH).
- D. Extreme care must be exercised in the use of preservatives so as not to cross-contaminate the samples. (i.e., nitric acid in samples for nitrogen species.)

5.5 Sample Identification

Each sample collected by KEMRON personnel should be clearly labeled with the following information, using water insoluble ink:

1. Client
2. Date and time
3. Sample source
4. Type of sample
5. Preservative used
6. Name of sampler
7. Analyses requested

Each laboratory should have labels printed with this information. Our clients should be supplied with these labels and encouraged to use them if they do not have their own.

5.6 Chain-of-Custody Procedures

Either the client or KEMRON may decide when chain-of-custody records are to be maintained for a sampling event. All official samples must be accompanied by chain-of-custody record sheets that includes the name of study, name of the client, the location, weather conditions, the date, the time, the sample number or other identification, the name of the sampler, the signature of the sampler, the preservatives used, and the analyses requested. When turning over possession of the

samples, the transferor and transferee sign (with date and time) on the record sheet. This record sheet allows the transfer of custody of a group of samples in the field to the laboratory. When a custodian transfers a portion of the samples to another person or laboratory, the individual samples must be noted. The laboratory personnel receiving the samples acknowledging receipt by signing in the appropriate column. Figure 5-1 gives an example of a KEMRON chain-of-custody record used for RCRA and NPDES water samples.

5.7 Field Notebooks

All field and laboratory personnel are required to maintain a bound and numbered field or laboratory notebook. The records for the smaller routine sampling projects conducted weekly or monthly should be kept in these notebooks.

- A. Use bound field notebooks to record field measurements and other pertinent information necessary to reconstruct the sample collection processes:
 1. Date and time
 2. Name of project manager
 3. Name of field assistants
 4. Note the weather condition
 5. Note all unusual circumstances surrounding the sampling areas
 6. Record all field measurements if done: flow, temperature, pH, specific conductance, chlorine residual, sulfite, etc.
- B. Maintain a separate set of field notebook for each major study and store them in a safe place where they may be protected and accounted for at all times.

6.0 SAMPLE HANDLING

6.1 General

The sample collector is responsible for the care and custody of the samples until the samples are properly transported to the receiving laboratory or given to an assigned custodian. Samples being transported in the KEMRON vans should be carefully packed in ice chests using foam dividers or other appropriate packaging materials. Ice or "Blue Ice" packs should be placed in each cooler to maintain the temperature below 4° C.

6.2 Logging

Upon receipt at the laboratory, the samples should be logged in the logbook as soon as possible, along with chain-of-custody forms when dealing with hazardous waste samples:

- A. Logbooks should be of the permanently bound hardback variety.

- B. All additions should be in permanent, water insoluble ink.
- C. Samples for a given client or special project should be logged as a group. On the left side of the logbook, the following information should be listed:

- 1. KEMRON Data No. - A number which is unique for each discreet sample source logged at a given KEMRON facility.

Example: WO52484-350

This data number is for sample No. 350 which was received on May 24, 1984, at the Williamstown, WV, facility. Separate aliquots with the different preservatives may be identified with letters:

Example: 84-350 A Cooled to 40 C
84-350 B HNO₃, pH <2, etc.

- 2. Client's Name
- 3. Sample Source - The client's sample identification
- 4. Date/Time Collected
- 5. All other information supplied on the sample label tag; plus unique observations about sample
- 6. Mode of delivery; date/time of sample receipt; who received
- 7. On the right side of the log page, the following information should be entered for each sample aliquot:

- a. Analyses requested
- b. Preservatives used

- D. A draft report for client is prepared with all of the information in [B] and [C] above which includes chain-of-custody forms and any other unique information attached to the received sample(s). This report is filled out as the analyses are completed and thus provides a means of monitoring the status of work in the laboratory.

6.3 Storage of Samples

- A. After a given analysis, the sample should be returned to the refrigerator if additional analyses are required or if holding time and volume would permit re-analysis.
- B. When holding times have expired and when all analyses have been completed, the samples are transferred to the shelves in the storage room. Samples are retained on the shelves for three weeks after report date, unless requested otherwise by the client.

6.4 Shipping Samples

Shipping samples from the field or from laboratory to laboratory is undesirable, but it is an unavoidable reality in many projects. Often the sampling sites are not within driving distance of our laboratories, and not all of our laboratories have full capabilities in the specialized areas of environmental analyses. Therefore, an effective system that both maintains the security and integrity of the sample and is cost effective must be followed for shipping intra-laboratory samples.

- A. Water samples should be packaged in heavy duty poly foam chests with corrugated cardboard covers.
- B. Samples should be wrapped with an appropriate packing foam, or separated by dividers.
- C. Samples should be pre-cooled to 4° C in a refrigerator before packing, and then an ice pack should be placed in each chest to maintain the temperature.
- D. Chain-of-custody records should accompany each set of samples shipped to another laboratory.
- E. Certain agencies or clients require strict adherence to chain-of-custody requirements related to assuring the integrity of the sample. In these cases, we should be prepared to ship samples in locked boxes, or use chain-of-custody seals on the sample bottles. The receiving laboratory must document that samples were received with the seals intact and samples were not altered.
- F. Samples should be shipped by UPS or other reputable carrier. Over night service is expensive, but may be necessary on samples with short holding times or those requiring priority turnaround.

7.0 CONTROL OF ANALYTICAL PERFORMANCE

7.1 General Analytical Chemistry

The main features of KEMRON's analytical quality assurance program are described in the sections which follow. Each of these features are standard in all KEMRON industrial hygiene and wastewater laboratories, and are effectively practiced for all applicable wet chemical or instrumental analytical methods.

7.1.1 Quality Assurance Coordinator

KEMRON has a full-time Quality Assurance Coordinator whose main responsibility is to develop and implement standard operating practice at all KEMRON laboratories. As a staff function independent of laboratory production, the QA coordinator works closely with the laboratory supervisors on all facets of data quality.

7.1.2 Quality Assurance Supervisor

Each analytical laboratory has a Quality Assurance Supervisor responsible for implementing the standard Quality Assurance Program.

7.1.3 Daily Quality Control Samples

Reference Standards

Midscale standards are analyzed with each batch of samples for all parameters. These QC checks are prepared separately and are independent of the standards used for calibration.

Duplicate Analyses

As a check on analytical precision for a given parameter, KEMRON performs duplicate analyses with each batch of samples analyzed. If KEMRON has responsibility for sampling in a given project, it will collect sufficient number and quantity of sample to analyze 10% in duplicate. For clients who perform their own sampling, we recommend that a definite schedule for duplicate analyses be practiced. Over a period of time, statistical data would become available for their specific matrix, which would provide a measure of the method precision and accuracy for that matrix.

Method Blank

A reagent or media blank is analyzed with each batch as a control over method contamination problems.

Matrix or Media Spikes

A matrix or media spike is analyzed with each batch of samples to provide long-term statistics for evaluating method accuracy in a wide range of matrix possibilities.

7.1.4 Quality Assurance Daily Reports

Whenever samples are analyzed, the quality control sample results are entered into the laboratory database. Reports are generated daily for review by the Quality Assurance Supervisor, the Quality Assurance Coordinator, and for management in general. Copies of the quality assurance daily report are available to the client by request. An example of the daily report is presented in Exhibit H (Table II).

7.1.5 Individual Analyst Notebooks

Each chemist maintains a bound and numbered laboratory notebook which includes records of methods development, standard preparation, as well as sample problems or observations, and parameter data in tabular form. Bench sheets are often used to supplement these books, when voluminous data are compiled. Data from the chemist's notebook and/or bench sheets are reviewed daily by supervisor prior to entry in the final database.

7.1.6 Individual Parameter Files

Raw data and final results for each parameter are maintained in two files within the laboratory. After initial review of bench sheets, the raw data are entered at the laboratory's computer with all calculation performed by electronic spreadsheets followed by automated storage in the parameter database. Hard copy printouts of raw and final results are placed in notebooks along with a copy of the pages from the chemist's notebook and/or bench sheets. The data, therefore, are easily accessible by computer terminal or manually in the parameter notebooks.

7.1.7 Independent Quarterly Audits

In addition to the analysis of its own quality assurance standards, KEMRON participates in an external quality assurance program on a regular basis. Quality assurance samples are acquired from EPA or private firms and analyzed as unknowns by our analysts on a monthly or quarterly basis. A report summarizing our performance in these audits is available upon request by our clients.

7.1.8 Statistics

KEMRON has established its Quality Assurance Program based on the statistics suggested in Standard Methods, ASTM Manual on Quality Control of Materials and the United States Environmental Protection Agency's publication, Handbook for Analytical Quality Control in Water and Wastewater Laboratories.

7.1.9 Control Limits

After sufficient data become available for a parameter, control charts and control limits are developed for method blanks, reference standards, duplicate analyses, and matrix spike analyses. The mean and standard deviation of each type of QC analysis (i.e., blank, standard, etc.) are used to establish warning limits at the 95% confidence level (+ two standard deviations) and absolute acceptance limits at the 99% confidence level:

$$\begin{aligned}\text{Upper Warning Limit} &= X + 2s \\ \text{Lower Warning Limit} &= X - 2s\end{aligned}$$

$$\begin{aligned}\text{Upper Acceptance Limit} &= X + 3s \\ \text{Lower Acceptance Limit} &= X - 3s\end{aligned}$$

where X = Mean
S = Standard Deviation

Initial Data and Construction of Control Charts:

In constructing an initial control chart, twenty consecutive data points are necessary. The time required to generate such a chart will vary with the frequency of the analysis (daily, weekly, monthly, etc.). Once these twenty data points are gathered, two control charts are constructed: (1) X Chart, Accuracy Control Chart, and (2) R Chart, Precision Control Chart. (See Exhibit G)

Subsequent Data:

The second phase in the Quality Assurance Program involves gathering and posting in the quality assurance notebooks twenty subsequent data points. This is done not only to control the accuracy and precision of current analyses, but also serves as a basis for constructing a new control chart for the next period. This method insures continued evaluation of laboratory and personnel performance.

7.2 Organic Analyses

The specialized techniques of gas chromatography and gas chromatography/mass spectrometry (GC/MS) require that special quality assurance program be developed for these areas. The general features of each of these programs are presented separately in this section.

7.2.1 Gas Chromatography

The KEMRON Environmental Services quality assurance program for analyses by gas chromatography is based on the recommendations in EPA's Handbook for Analytical Quality Control in Water and Wastewater Laboratories (EPA-600/4-79-019) and Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater (EPA-600/4-82-057). The main features of our GC quality control program are summarized below:

.Reagents and Solvents

Use of the highest quality reagents and solvents available for organic residue analysis.

.Standards

Separate standards for instrument calibration and quality control (spike) samples.

.Method Blanks

Analysis of a deionized water method blank with each batch of samples.

.Identifications

Qualitative confirmation by spiking with the suspected pollutant or by analysis on a second GC column.

.Spiked Samples

Analysis of a spiked sample or deionized water spike with each batch of samples.

.Control Limits

Establishment of statistical control limits for each parameter for which spiked recovery data is available. This is accomplished by the calculation of a mean percent recovery (R) and the standard deviation(s) of the percent recovery for each parameter after sufficient data points (5) have been obtained. Upper and lower control limits are calculated as follows:

$$\text{Upper Control Limit (UCL)} = R + 3s$$

$$\text{Lower Control Limit (LCL)} = R - 3s$$

.Quarterly Audits

Analysis of EPA Quality Control samples on a quarterly basis to further test the proficiency of our analysts.

.Customized QA

For the specific project needs of any client, KEMRON will custom design its quality assurance routine with regard to blanks, duplicates, spikes or other QC procedures.

7.2.2 Gas Chromatography/Mass Spectrometry (GC/MS)

KEMRON uses well established standard analytical methods for the analysis of organic compounds by GC/MS. For the analysis of priority pollutants in water, KEMRON uses EPA Methods 624 and 625 as revised in Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater (EPA-600/4-82-057, July 1982). The quality assurance features summarized below adhere strictly to the requirements and recommendations presented in this EPA publication.

Daily Autotune Report

Each day that samples are analyzed, the mass spectrometer is autotuned with PFTBA using ion masses of 69, 219, and 502 amu. The autotune results are included in analytical report.

BFB Criteria Test

The performance of the GC/MS system is checked out daily for volatile organic analyses (VOA) by injecting the instrument with BFB (bromofluorobenzene). The relative abundances of key ions are compared, and the instrument is adjusted until the prescribed criteria are met.

DFTPP Criteria Test

Prior to Base/Neutral or Acid Fraction analyses, the GC/MS instrument is certified according to EPA protocol by injecting with DFTPP (decafluorotriphenylphosphine) and comparing the relative ion abundances for key ions. The instrument is adjusted until the criteria are met.

Method Blanks

A sample of organic-free water is analyzed with each batch of samples to monitor for possible contamination in solvents, reagents, glassware, or laboratory environment.

Matrix Spikes

A control sample prepared by spiking organic-free water or a second aliquot of a sample matrix with a representative number of compounds from each priority pollutant fraction is analyzed with each batch of samples.

Surrogate Spikes

All samples are spiked with the EPA method specified surrogate standards - four surrogates in the VOA fraction, two in the base neutral fraction, and one in the acid extractable (phenols) fraction. Results of the surrogate spikes are provided in the QA section of the analytical reports.

.Control Charts

Percent recovery data derived from the matrix surrogate spike are used to construct control charts for each surrogate.

.Duplicate Analyses

Laboratory and field replicates are also analyzed routinely to validate the precision of the sampling technique and the precision of the analysis.

7.3 Data Validation

7.3.1 Data Reduction

KEMRON automates data calculations and reduction as much as possible by using IBM compatible personal computers and electronic spreadsheet software. Most analyses have been programmed to allow for raw data entry and editing at the keyboard, with integrated software performing all calculations and permanent database generation for the individual parameter data. Data entry errors are checked by comparing the raw data printouts to the chemist's original work, and the common sources of error in data reduction are eliminated entirely. Raw and final data are stored on internal fixed disk, with either magnetic tape or flexible disk as backup. Eventually all analyses will be programmed into the laboratory database, but until such time, one of the following procedures may also be used to calculate test results:

- A. Data from simple analytical procedures such as gravimetric and titrimetric procedures are converted into final form by means of Hewlett-Packard desk calculators. Calculations which involve several steps are usually handled by programs stored on magnetic cards using the Hewlett-Packard Model 97A desk calculator. One or two step calculations are performed manually by the technician and final data recorded in parameter notebooks.
- B. Visible spectrophotometric results are computed from a calibration curve produced by a curve fitting program on the HP 97. The curves are stored on magnetic cards, and the technician need only enter the correct absorbance value and the parameter concentration is displayed. Corrections for concentration or dilution factors must be computed manually.
- C. Atomic absorption spectrophotometers are calibrated to display direct concentrations whenever possible. Some analyses such as mercury require the analyst to construct calibration curves using absorbance vs concentration. Other determinations, such as those using standard additions, require manual computation with calculators to generate final results.

- D. All KEMRON gas chromatographs (GC), liquid chromatographs (LC), and gas chromatograph/mass spectrometer (GC/MS) are equipped with programmable data systems which allow for automatic generation of parameter data in its final reported form. All calculations by the analyst are eliminated when the data systems are programmed to their full capabilities.

7.3.2 Review and Validation

When analyses are completed by the analyst, raw data and final results are immediately reviewed by the laboratory supervisor. The raw data from chemist's notebooks or bench sheets include all of the analytical variables compiled for samples, replicates, blanks, standards, and matrix spikes. Data assessment passes through the following stages:

- I. First, the results of blanks, standards, replicates and spikes are compared to existing control charts to evaluate the overall data quality. The laboratory supervisor also reviews the QC data for trends (five consecutive analyses showing successive increases or decreases in value) or shifts (seven successive points on the same side of the accepted value for the reference standard).
- II. After the initial QA review, a preliminary report is generated for each sample. It is again reviewed by the laboratory supervisor who evaluates the data for the following:
 - .Significant figures
 - .Detection limits
 - .Credibility, i.e., results in expected or historical ranges
 - .Related data compatibility
 - .Anion/Cation balances
 - .BOD/COD relationships, etc.
- III. A final draft of the sample report is typed and is compared to the rough draft in II, either by the Regional Manager or Project Manager. It is also reviewed at that time for completeness of sample data, QC data, chain-of-custody forms, attachments, and other proposal requirements or contract agreements.

7.3.3 Corrective Action

An out of control situation exists when the results of the blank, standard, sample replicate, or spike recovery analyses are beyond the acceptance limits (usually three standard deviations or 99% confidence level). If either the blank or reference standard is out of control, the data from that analytical run are judged invalid. An investigation to find the cause of problem is undertaken by the analyst and laboratory supervisor and a Quality Assurance Action Report is initiated. After the problem has been corrected, as verified by acceptable performance on blanks and standards, the analyses for the batch in question are repeated.

A situation also demanding corrective measures exists when quality assurance data for blanks, standards, sample replicates or matrix spikes are reported beyond the warning limits (two standard deviations), or a trend or shift is observed for the reference standard. In this case, samples need not be re-analyzed, provided the data are within acceptance limits. However, a Quality Assurance Action Report is initiated by the analyst and laboratory supervisor and correction action must be taken before another batch of samples is analyzed by that method. If the situation recurs with the next batch of samples, then an out-of-control situation exists at that time.

Whenever replicate analysis (precision) data or matrix spike recovery (accuracy) data are out of acceptance limits, comprehensive corrective action (batch re-analysis) may not be necessitated. Often, these problems can be attributed to matrix effect. If the remaining QC data (method blank and reference standard) are in control, then the only corrective action implied is re-analysis of the sample in question - this only to verify the matrix effect or other specific interference problems. Whenever a matrix effect is confirmed, the method of standard addition is used for quantification, if applicable to the analysis method.

8.0 STANDARDS, CALIBRATION, AND INSTRUMENTATION

8.1 General

Since the modern analytical laboratory depends heavily upon instrumentation, their calibration, operation, and maintenance must be a primary concern in the production of satisfactory data. The instruments commonly used in KEMRON water and industrial hygiene laboratories include the following: ,

- Analytical balance
- pH/Selective-ion meters
- Conductivity meter
- Turbidimeter
- Spectrophotometers (visible, ultraviolet (UV),
infrared (IR), and Atomic absorption (AA)
- Gas chromatographs (GC)
- Liquid chromatographs (LC)
- Gas chromatograph/mass spectrometers (GC/MS)

In the sections that follow the general requirements for calibration, operation and maintenance of these instruments is presented.

8.2 Instrument Logs

Every analytical instrument in the laboratory which requires calibration and/or maintenance to generate reliable data must have a logbook. The instrument logbook should be bound variety and begin with the initial installation and set-up procedures performed by the instrument field engineers. All daily operational notes, problems, routine maintenance procedures, instrument zero and calibration set points, calibration data, and repair notes should be a permanent part of the instrument log. The oven and/or refrigerator temperatures are recorded in a bound and numbered notebook.

8.3 Calibration Standards

The accuracy of data produced from analytical instrumentation depends to a large degree on the quality of calibration standards. KEMRON uses fully documented procedures to assure that calibration standards are prepared with, or can be traced to the highest standard of quality available for a particular analyte.

8.3.1 Concentrated Stock Standards

Concentrated stocks are prepared using Standard Reference Materials, primary standards, or reagents of known purity as specified in 3.4.1. They are prepared gravimetrically using an analytical balance with a precision of ± 0.1 mg.

Rev. 2/86

Records of ALL stock standards are to be maintained in two places:

1. The chemist's notebook
2. The KEMRON Standards Logbook

The KEMRON Standards Logbook provides documentation for all the pertinent data needed to verify the concentration of the stock standard. An example of the documentation provided by these forms is presented in Exhibit I.

Each stock solution is assigned a unique number. An example will serve to illustrate the number system:

S16021705

S: indicates that it is a concentrated stock
1: prepared at the Baton Rouge facility
6: prepared in 1986
0217: prepared on February 17
05: was the 5th stock prepared on that day

Each stock solution is provided with a label with the following minimum information:

1. Stock number
2. Chemist's initials
3. Parameter
4. Concentration
5. Units
6. Expiration date

The laboratory supervisor is responsible for weekly reviewing of the KEMRON Standards Logbook to verify the accuracy of standards preparation and expiration dates.

The expiration date for concentrated stocks is established from the shelf life specified by the standard method. Regardless of the stability of a parameter, fresh stock solutions are prepared at least once yearly.

Verification of a fresh stock's concentration is accomplished by performing side-by-side analyses on both the old and new standards. After verification of concentration, the expired stock solutions may be discarded.

8.3.2 Intermediate Stock Standards

For many analyses, it is not advisable to prepare the working standards in a single serial dilution from the stock. Intermediate stock standards are used in these analyses and their preparation and traceability are also documented in the KEMRON Standards Logbook. Exhibit I lists an example of the logbook's format and contents.

Rev. 2/86

Only Class A volumetric glassware may be used to prepare the intermediate stocks by the serial dilution procedure.

8.3.3 Working Standards

Standards which are used to calibrate the analysis system are called the working standards. They are prepared by serial dilution of the concentrated or intermediate stock standards using only Class A volumetric glassware. The KEMRON Standards Logbook is used to verify the working standards concentration and traceability to concentrated stocks. (See Exhibit I for an example logbook form.)

Rev. 2/86

8.4 Preventive Maintenance

A detailed treatment of instrumental servicing and maintenance is beyond the scope of this manual. All instruments in the laboratory undergo regular maintenance, calibration, and performance checks on a daily, weekly, or monthly basis, depending on the guidelines specified in the manufacturers instrument manual and the requirements of the standard methods employed. Instrument maintenance checklists should be developed and kept up to date for all refrigerators, ovens, desiccators, laboratory balances, pH meters, spectrophotometers, gas chromatographs, etc. A few selected topics of particular interest will be covered in the sections that follow.

8.5 Analytical Balance

The most important piece of equipment in any analytical laboratory is the analytical balance. The accuracy of data related to weight-prepared standards can be no better than that of the analytical balance. For this reason, proper care and use of the analytical balance must be of highest priority, the following should be standard operating requirements in each KEMRON facility.

- A. Analytical balances should be mounted on a heavy, shock-proof table, constructed of either marble or concrete, and placed in an area of low traffic. The balance level should be checked daily and adjusted when necessary.
- B. Balances must be protected from extreme temperature and humidity change. A beaker of silica gel desiccant should be placed in the balance and changed frequently.
- C. When not in use, the beam should be raised from the knife edges, and all weights returned to the beam.
- D. All spills on the pan or inside the balance must be avoided, and the balance must be kept scrupulously clean at all times.

- E. Balances will be checked and adjusted at least twice a year by a company serviceman or balance specialist. A service contract and maintenance schedule is also recommended.

Calibration

1. Standardized weights, traceable to the National Bureau of Standards, must be available for checking the performance of the balance.
2. After following the manufacturers requirements for internal calibration and taring, an initial weight is placed on the pan and the balance is again tared. A second weight of 100 mg is placed on the balance pan and the weight determined to the nearest 0.1 mg. An absolute error of 0.2 mg should not be exceeded for most modern electronic balances. This procedure should be repeated with another weight to assure linearity and accuracy throughout the weight range of interest.

The Balance Logbook

All maintenance and service records should be entered in the logbook. The daily calibration records should include the date, time, the initials of the operator, and the weights for at least two standard checks using the procedure described earlier.

9.0 TRAINING OF LABORATORY PERSONNEL

9.1 General

The topics and their sequence for the training of new laboratory technicians, analysts, and chemists are presented in this section. KEMRON management believes that each analyst should be thoroughly trained and fully understand the assignments of his job before taking on additional responsibilities. Since analytical operations in the laboratory can be graded according to the degree of complexity, all analysts, sub-professional or professional, should be thoroughly instructed in basic laboratory operations, the rate varying according to the degree of professional maturity. Some of the basic operations and a recommended order for training will follow.

9.2 General Orientation

Become familiar with general company policy, structure and functions.

9.3 Safety Policy

9.4 Quality Assurance Manuals

This manual and other KEMRON SOP's should be read before beginning laboratory operations.

9.5 Data Handling and Report

Analyst should become familiar with reporting formats, reporting limits, significant figures, parameter notebooks, quality assurance notebooks, and quality assurance daily reports.

9.6 Sample Logging and Handling

Routine procedure for recording of samples entering the laboratory and the assignment of this responsibility will be emphasized. The procedure for routing of the samples to the analyst should be covered. The storage, preservation, and holding times of samples should be included at this point.

9.7 Measuring

The new analysts, especially non-degree laboratory technicians, should be instructed on the use of volumetric glassware. The correct use of pipets, burets, and graduates should be emphasized.

9.8 Weighing

Because the accuracy of almost every analytical method is related to a weighing operation, the proper training on the analytical balance should occur early and be emphasized strongly. The correct use of the analytical balance is discussed more fully in Section 8.5.

LIST OF EXHIBITS

LIST OF EXHIBITS

- A. Analytical Methods, References
- B. Sample Preservation, Minimum Volumes, Maximum Holding Times
- C. Chain-of-Custody Records
- D. Example KEMRON Bottle Tags and Labels
- E. QA Statistics Formula and Example Calculation
- F. Example Pages from KEMRON Quality Assurance Notebook
- G. Example Control Charts for Precision and Accuracy
- H. Example Quality Assurance Reports
 - QA Daily Report to Management/Client
 - QA Violation Report
- I. Calibration Standards Logbook Forms
- J. Example KEMRON Sample Shipping Log
- K. KEMRON Analytical Reporting Format
 - Inorganic Analyses
- L. KEMRON Analytical Reporting Format
 - GC/MS Analyses

EXHIBIT A

Analytical Methods and References

ANALYTICAL METHODS

<u>WATER QUALITY ANALYSES</u>	<u>REFERENCE</u>	<u>METHOD NO.</u>
Acidity	(1) f	305.1
Alkalinity (Phenolphthalein)	(4)	403
Alkalinity (Phenolphthalein and Total)	(4)	403
Alkalinity (Total)	(1)	310.1
Bicarbonate	(4)	403
Biochemical Oxygen Demand, 5-Day	(1)	405.1
Boron (Colorimetric)	(1)	212.3
Bromide (includes Iodide)	(1)	320.1
Carbonate	(4)	403
Chemical Oxygen Demand	(10)	
Chloride	(1)	325.3
Chlorine		
Residual, Total	(1)	330.3
Color	(1)	110.2
Cyanide		
Amenable to Chlorination	(1)	335.1
Free		
Total	(1)	335.2
Dissolved Oxygen	(1)	360.1
Fluoride (No Distillation)	(1)	340.2
Fluoride (Distillation)	(1)	340.2
Hardness	(1)	130.2
Iodide	(1)	345.1
Nitrogen		
Ammonia (Distillation)	(1)	350.2
Kjeldahl, Total	(1)	351.3
Nitrate	(1)	353.3
Nitrite	(1)	354.1
Nitrate-Nitrite	(1)	353.3
Organic	(1)	351.3
Oil and Grease		
Freon Extractables	(1)	413.1
Infrared	(1)	413.2
Petroleum Hydrocarbons		
Infrared	(1)	418.1
pH	(1)	150.1
Phenolics	(1)	420.1
Phosphorus		
Orthophosphate	(1)	365.2
Total	(1)	365.2
Thiocyanate	(6) 15th Ed.	412K

Water Quality Analyses (Continued)

	<u>REFERENCE</u>	<u>METHOD NO.</u>
Settleable Matter	(1)	160.5
Silica	(1)	370.1
Specific Conductance	(1)	120.1
Solids		
Filterable (Dissolved)	(1)	160.1
Non-Filterable (Suspended)	(1)	160.2
Total	(1)	160.3
Volatile (includes either TSS, TS, or TDS)	(1)	160.4
Sulfate	(1)	375.4
Sulfide	(1)	376.1 & 376.2
Sulfite	(1)	377.1
Surfactants	(1)	425.1
Total Organic Halides (TOX)	(5)	450.1
Total Organic Carbon	(1)	415.1
Turbidity	(1)	180.1

BACTERIOLOGICAL

Coliform		
Fecal (Membrane Filter)	(4)	909C
Total (Membrane Filter)	(4)	909A
Total (MPN)	(4)	908A
Fecal (MPN)	(4)	908C

TRACE METAL ANALYSES (Atomic Absorption)

Aluminum	(1)	202.1
Antimony	(1)	204.2
Arsenic	(1)	206.2
Barium	(1)	208.1
Beryllium	(1)	210.1
Cadmium	(1)	213.1
Calcium	(1)	215.1
Chromium, Hexavalent	(1)	218.4
Chromium, Total	(1)	218.1 & 218.2
Cobalt	(1)	219.1
Copper	(1)	220.1
Iron	(1)	236.1
Lead	(1)	239.1 & 239.2
Lithium	(1)	
Magnesium	(1)	242.1
Manganese	(1)	243.1
Mercury (Cold Vapor)	(1)	245.1
Molybdenum	(1)	246.1
Nickel	(1)	249.1
Chromium, Hexavalent	(4)	312 B

Trace Metal Analyses (Atomic Absorption) (Continued)

	<u>REFERENCE</u>	<u>METHOD NO.</u>
Potassium	(1)	258.1
Selenium	(1)	270.2
Silver	(1)	272.1
Sodium	(1)	273.1
Tellurium	-	
Thallium	(1)	279.2
Tin	(1)	282.1 & 282.2
Titanium	(1)	283.1 & 283.2
Vanadium	(1)	286.1 & 286.2
Zinc	(1)	289.1

HAZARDOUS WASTE ANALYSES

Sample Preparation		
Filtration	(7)	-
Extraction	(7)	-
Compositing	(7)	-
Corrosivity	(7)	-
Ignitability	(7) (8)	ASTM D93-79
Reactivity		
EP Toxicity		
Extraction	(7)	
Metals		
Arsenic	(1)	206.2
Barium	(1)	208.1
Cadmium	(1)	213.1
Chromium	(1)	218.1
Lead	(1)	239.1
Mercury	(1)	245.1
Selenium	(1)	270.2
Silver	(1)	272.1
Organics		
Pesticides	(2)	-
Endrin, Lindane, Methoxychlor, Toxaphene		
Herbicides	(2)	-
2,4,D; 2,4,5-TP (Silvex)		
PCB's		
pH	(1)	
Phosphorous		
Specific Gravity		
Total Solids		
Ash Content		

Hazardous Waste Analyses (Continued)

	<u>REFERENCE</u>	<u>METHOD NO.</u>
Halogens (TOX Screen)	(5)	450.1
Sulfur		
BTU Content		
Viscosity		
Cyanide	(7)	
Phenolics	(7)	
<u>TRACE ORGANIC PARAMETERS IN DRINKING WATER</u>		
Pesticides	(2)	
Endrin, Lindane, Methoxychlor, Toxaphene		
Herbicides	(2)	
2,4-D; 2,4,5-TP (Silvex)		
Total Organic Halides (TOX)	(5)	450.1
<u>RADIOLOGICAL</u>		
Gross Alpha and Beta	(4)	703
Radium 226	(12)	903.0
Radium 228	(12)	904.0
<u>PRIORITY POLLUTANT ORGANIC PARAMETERS</u>		
Volatile Organics	(13)	624
(31 Compounds)		
Acid Extractables	(13)	625
(11 Compounds)		
Base-Neutral	(13)	625
(46 Compounds)		
Pesticide and PCB	(13)	625
(26 Compounds)		

TABLE I (Cont.)
QUALITY ASSURANCE NOTEBOOKS

Sample Identification: TOC and Date	Quality Assurance Reference Standards		Range (Ri)	Average Found	Set-Up By	Analyzed By	Comments
	Actual (\bar{X})	Actual Found					
4/25	121	124	4	122			
	121	120					
4/26	121	121	2	120			
	121	119					
4/27	121	124	4	122			
	121	120					
4/28	121	122	0	122			
	121	122					
4/29	121	126	2	127			
	121	128					
4/30	121	120	2	119			
	121	118					

EXHIBIT G

Example KEMRON Control Chart
for
Precision and Accuracy

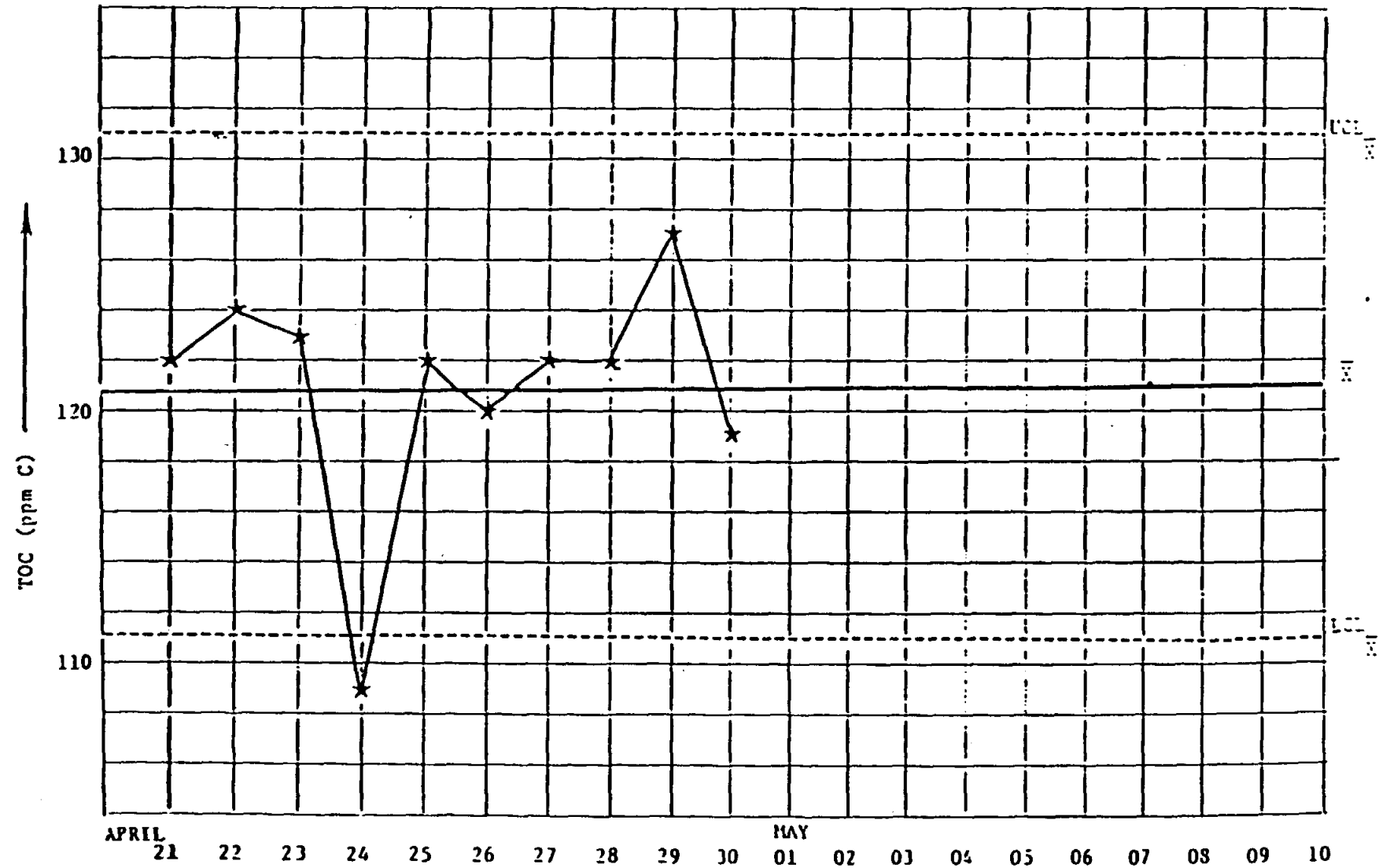


FIGURE 1. \bar{X} CHART
95% CONFIDENCE

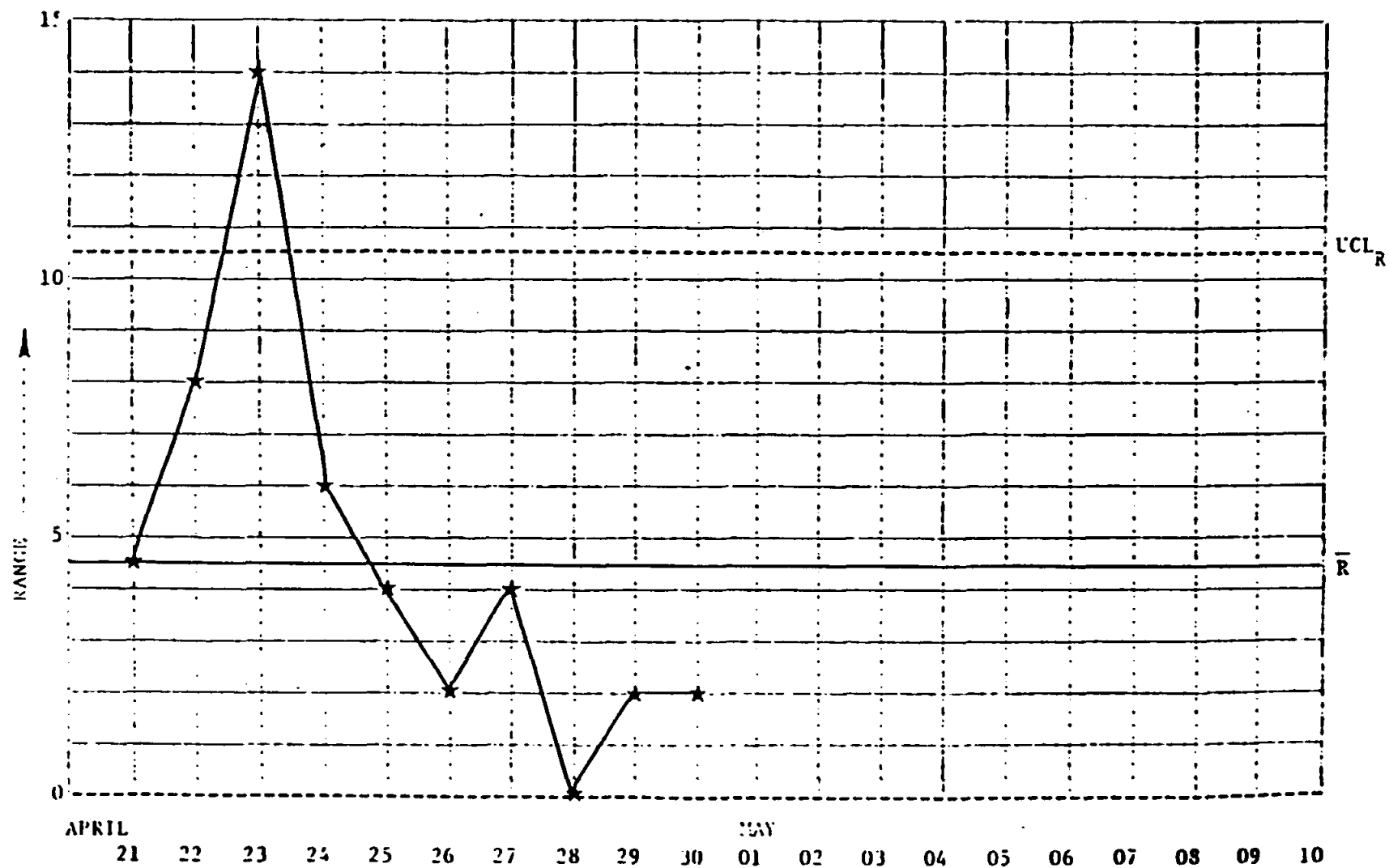


FIGURE 2. R CHART
95% CONFIDENCE

EXHIBIT H

Example of Quality Assurance Reports to Management

QA Daily Report

QA Violation Reports

QUALITY ASSURANCE DAILY REPORT

Laboratory: Ohio Valley

Date: 02/12/86

Parameter	Units	Analyst	REFERENCE STANDARD				DUPLICATE SAMPLE		Range	UCLr
			Known	Result	UCLx	LCLx	Result1	Result2		
Selenium	ppb	BY	100	97	112	92	0.05	0.05	0	*
Lead	ppb	BY	100	98	108	88	0	0	0	*
Boron	ppm	RS	0.5	0.55	*	*	43	45	2	*
Conductivity	uS/m	BC	100	98	106	89	110	110	0	*
Nitrite	ppm	RS	0.1	0.091	0.11	0.096	0.013	0.013	0	*
Nitrate	ppm	RS	0.25	0.25	0.28	0.24	3	2.7	0.3	*
Phenol	ppb	JM	10	9.4	10.9	8.6	--	--	0	*
Phenol	ppm	JM	0.5	0.48	0.56	0.46	0.005	0.009	0.004	*
BOD	ppm	BC	210	170	240	130	140	140	0	*
TOC	ppm	HG	121	124	129	108	122	125	3	*

UCLx = Upper Control Limit (Standard)

LCLx = Lower Control Limit (Standard)

UCLr = Upper Control Limit (Range)

* = Initial Data Collection

"0" = Below Detection Limits

QUALITY ASSURANCE DAILY REPORT

Laboratory: Ohio Valley

Date: 02/12/86

METHOD BLANK				MATRIX/MEDIA SPIKE					
Parameter	Units	Analyst	Result	UCLb	Conc.	Recovery	Rec. (%)	UCLs (%)	LCLs (%)
Selenium	ppb	BY	0	*	100	98	98	*	*
Lead	ppb	BY	0	*	100	90	90	*	*
Boron	ppm	RS		*	0.5	0.53	106	*	*
Conductivity	mS/m	BC	0	*	100	92	92	*	*
Nitrite	ppm	RS	0	*	0.1	0.093	93	*	*
Nitrate	ppm	RS	0	*	0.25	0.22	88	*	*
Phenol	ppm	JM		*	0.5	0.44	88	*	*
BOD	ppm	BC	2.3	*	210	150	71	*	*

UCLb = Upper Control Limit (Blank)

UCLs = Upper Control Limit (Spike Recovery)

LCLs = Lower Control Limit (Spike Recovery)

* = Initial Data Collection

"0" = Below Detection Limits

QUALITY ASSURANCE ACTION REPORT

1. Date:
2. Laboratory:
3. Supervisor:
4. Analyst:
5. Parameter:
6. Blank Result: UCLb:
Standard Result: UCLx: LCLx:
Duplicate Results: UCLr:
Spike Level: Percent Rec: UCLs: LCLs:
7. Analyst's Description of Problem:
8. Comments of Q.A. Supervisor:
9. Action Taken to Solve Problem:
10. Were Analyses Repeated?
 - A. If so, give results for: Reagent Blank:
Standard:
 - B. If not, reason:

EXHIBIT I

Standard Log Forms for:

Concentrated Stock Standards

Intermediate Standards

Working Standards

PREPARATION OF CONCENTRATED STOCK STANDARDS

Page _____

No. S _____ Parameter _____ Chemist _____
Compound _____ Lot No. _____ Purity _____ %
Final gross wt. _____ g Dilution Volume _____
* Tare wt. _____ g Concentration _____
Net wt. _____ g Date Prepared _____
** Adj. Net wt. _____ mg Expiration Date _____

No. S _____ Parameter _____ Chemist _____
Compound _____ Lot No. _____ Purity _____ %
Final gross wt. _____ g Dilution Volume _____
* Tare wt. _____ g Concentration _____
Net wt. _____ g Date Prepared _____
** Adj. Net wt. _____ mg Expiration Date _____

No. S _____ Parameter _____ Chemist _____
Compound _____ Lot No. _____ Purity _____ %
Final gross wt. _____ g Dilution Volume _____
* Tare wt. _____ g Concentration _____
Net wt. _____ g Date Prepared _____
** Adj. Net wt. _____ mg Expiration Date _____

No. S _____ Parameter _____ Chemist _____
Compound _____ Lot No. _____ Purity _____ %
Final gross wt. _____ g Dilution Volume _____
* Tare wt. _____ g Concentration _____
Net wt. _____ g Date Prepared _____
** Adj. Net wt. _____ mg Expiration Date _____

* Wt. of empty boat

** Corrected for purity or % composition

No. <u>I</u>	Parameter _____	Chemist _____
Parent Stock <u>S</u>		Final Concentration _____
Parent Stock Conc. _____		Units _____
Aliquot of Parent Stock _____	ml	Preparation Date _____
Dilution Volume _____	ml	Expiration Date _____

No. <u>I</u>	Parameter _____	Chemist _____
Parent Stock <u>S</u>		Final Concentration _____
Parent Stock Conc. _____		Units _____
Aliquot of Parent Stock _____	ml	Preparation Date _____
Dilution Volume _____	ml	Expiration Date _____

No. <u>I</u>	Parameter _____	Chemist _____
Parent Stock <u>S</u>		Final Concentration _____
Parent Stock Conc. _____		Units _____
Aliquot of Parent Stock _____	ml	Preparation Date _____
Dilution Volume _____	ml	Expiration Date _____

No. <u>I</u>	Parameter _____	Chemist _____
Parent Stock <u>S</u>		Final Concentration _____
Parent Stock Conc. _____		Units _____
Aliquot of Parent Stock _____	ml	Preparation Date _____
Dilution Volume _____	ml	Expiration Date _____

PREPARATION OF WORKING STANDARD SOLUTIONS

No. <u>W</u>	Analysis _____	Chemist _____				
	Parameter	Parent Solution Number	Conc. of Par. Sol.	Aliq. Vol.	Dil. Vol.	Final Concentration Units: _____
1.	_____	_____	_____	_____	_____	_____
2.	_____	_____	_____	_____	_____	_____
3.	_____	_____	_____	_____	_____	_____
4.	_____	_____	_____	_____	_____	_____
5.	_____	_____	_____	_____	_____	_____
6.	_____	_____	_____	_____	_____	_____
7.	_____	_____	_____	_____	_____	_____
8.	_____	_____	_____	_____	_____	_____
9.	_____	_____	_____	_____	_____	_____
10.	_____	_____	_____	_____	_____	_____

Preparation Date _____ Expiration Date _____

No. <u>W</u>	Analysis _____	Chemist _____				
	Parameter	Parent Solution Number	Conc. of Par. Sol.	Aliq. Vol.	Dil. Vol.	Final Concentration Units: _____
1.	_____	_____	_____	_____	_____	_____
2.	_____	_____	_____	_____	_____	_____
3.	_____	_____	_____	_____	_____	_____
4.	_____	_____	_____	_____	_____	_____
5.	_____	_____	_____	_____	_____	_____
6.	_____	_____	_____	_____	_____	_____
7.	_____	_____	_____	_____	_____	_____
8.	_____	_____	_____	_____	_____	_____
9.	_____	_____	_____	_____	_____	_____
10.	_____	_____	_____	_____	_____	_____

Preparation Date _____ Expiration Date _____

EXHIBIT J

KEMRON Sample Shipping Log

Number _____

III-KEMRON
Sample Out Log-Form

Telephone No. (204) 375-5800

Date Shipped _____

IHI KEMRON

To _____

901 Highland Ave.

Williamstown, WV 26107

Date Received _____

Received By _____

 UPS Purolator Bus

Chain of Custody Forms Attached

Charged _____

Return Sample Kits

Approved _____

[illegible]

Please Sign and Return One Copy

Sarah Vandenberg
Sarah Vandenberg
Laboratory Supervisor

EXHIBIT K

**KEMRON Analytical Reporting Format
Inorganic Analyses**

ANALYTICAL REPORT

Client:

Report Date: 03/04/86

Report Number:

Purchase Order No.:

Attn:

Collected By:

Kemron Sample No.:

Date Received:

Sample Source: Composite Effluent

PARAMETER	UNITS	RESULTS	ANALYST/DATE/TIME
pH	20 Degrees C	6.9	RS/02/06/1630
Biochemical Oxygen Demand	mg/l O2	580	BC,RS/02/07/1500
Chemical Oxygen Demand	mg/l O2	1,100	RS/02/13/0845
Total Organic Carbon	mg/l C	320	HG/02/12/2040
Total Suspended Solids	mg/l	110	BC/02/07/0820
Nitrogen, Ammonia	mg/l N	35	JM/02/17/0930
Chromium, Total	mg/l Cr	<0.05	RS/02/18/1545
Copper, Total	mg/l Cu	0.02	BY/02/20/1015
Lead, Total	mg/l Pb	<0.05	BY/02/18/1500
Nickel, Total	mg/l Ni	0.04	BY/02/20/0945
Zinc, Total	mg/l Zn	5.0	BY/02/20/0900

Approved By:

Sarah Vandenberg
Sarah Vandenberg
Laboratory Supervisor

EXHIBIT L

**KEMRON Analytical Reporting Format
GC/MS Analyses**

ANALYTICAL REPORT

For:

ABC Company
0000 First Street
Marietta, OH 45750

Attn: Joe White

Sample Source:

Date Received:

KEMRON Sample No.: 0000000

Purchase Order No.: 0000

Submitted By:

KEMRON ENVIRONMENTAL SERVICES
901 Highland Avenue
Williamstown, WV 26187

January 1, 1986

Approved By:

Sarah Vandenberg
Laboratory Supervisor

GC/MS FRACTION-VOLATILE COMPOUNDS

Kemron Sample No.:

Sample Source:

COMPOUND	CONCENTRATION (UG/L)	DETECTION LIMIT (UG/L)
1V. Acrolein	BDL	5000
2V. Acrylonitrile	BDL	5000
3V. Benzene	BDL	500
4V. Bis (Chloromethyl) Ether	BDL	500
5V. Bromoform	BDL	500
6V. Carbontetrachloride	BDL	500
7V. Chlorobenzene	5,500	500
8V. Chlorodibromomethane	BDL	500
9V. Chloroethane	BDL	500
10V. Chloroethylvinyl Ether	BDL	500
11V. Chloroform	BDL	500
12V. Dichlorobromomethane	BDL	500
13V. Dichlorodifluoromethane	BDL	500
14V. 1,1-Dichloroethane	BDL	500
15V. 1,2-Dichloroethane	BDL	500
16V. 1,1-Dichloroethylene	BDL	500
17V. 1,2-Dichloropropane	BDL	500
18V. 1,2-Dichloropropylene	BDL	500
19V. Ethylbenzene	BDL	500
20V. Methyl Bromide	BDL	500
21V. Methyl Chloride	BDL	500
22V. Methylene Chloride	BDL	500
23V. 1,1,2,2-Tetrachloroethane	BDL	500
24V. Tetrachloroethylene	BDL	500
25V. Toluene	BDL	500
26V. 1,2-Trans-Dichloroethylene	BDL	500
27V. 1,1,1-Trichloroethane	BDL	500
28V. 1,1,2-Trichloroethane	BDL	500
29V. Trichloroethylene	BDL	500
30V. Trichlorofluoromethane	BDL	500
31V. Vinyl Chloride	BDL	500

BDL: Below Detection Limit

Date Analyzed: 02/06/86 By: Seshu Chalasani

Time of Analysis: 0110

Comments:

The sample was exhibiting strong smell of organics and was diluted to 1:50. Hence, the detection limits are high.

GC/MS FRACTION-ACID COMPOUNDS

Kemron Sample No.:

Sample Source:

COMPOUND	CONCENTRATION (UG/L)	DETECTION LIMIT (UG/L)
1A. 2-Chlorophenol	BDL	2,000
2A. 2,4-Dichlorophenol	BDL	2,000
3A. 2,4-Dimethylphenol	BDL	2,000
4A. 4,6-Nitro-O-Cresol	BDL	10,000
5A. 2,4-Dinitrophenol	BDL	10,000
6A. 2-Nitrophenol	BDL	2,000
7A. 4-Nitrophenol	BDL	2,000
8A. p-Chloro-m-Cresol	BDL	2,000
9A. Pentachlorophenol	BDL	2,000
10A. Phenol	BDL	2,000
11A. 2,4,6-Trichlorophenol	BDL	2,000

BDL: Below Detection Limit

Date Extracted: 02/03/86 By: Sayi Malineni

Date Analyzed: 02/05/86 By: Seshu Chalasani

Time of Analysis:

Comments:

The sample was dark brown in color and exhibited strong odor of organics. Only 50 ml of the sample was processed for extraction. The organic extract was again dark in color and was diluted to 10 ml, Accordingly, the detection limits are high.

GC/MS FRACTION-BASE/NEUTRAL COMPOUNDS

Part I

Kemron Sample No.:

Sample Source:

COMPOUND	CONCENTRATION (UG/L)	DETECTION LIMIT (UG/L)
1B. Acenaphthene	BDL	2,000
2B. Acenaphthylene	BDL	2,000
3B. Anthracene	BDL	2,000
4B. Benzidine	BDL	2,000
5B. Benzo(a)Anthracene	BDL	2,000
6B. Benzo(a)Pyrene	BDL	2,000
7B. 3,4-Benzofluoranthene	BDL	2,000
8B. Benzo(ghi)Perylene	BDL	2,000
9B. Benzo(k)Fluoranthene	BDL	2,000
10B. Bis(2-Chloroethoxy)Methane	BDL	2,000
11B. Bis(2-Chloroethyl)Ether	BDL	2,000
12B. Bis(2-Chloroisopropyl)Ether	BDL	2,000
13B. Bis(2-Ethylhexyl)Phthalate	BDL	2,000
14B. 4-Bromophenyl Phenyl Ether	BDL	2,000
15B. Butyl Benzyl Phthalate	BDL	2,000
16B. 2-Chloronaphthalene	BDL	2,000
17B. 4-Chlorophenyl Phenyl Ether	BDL	2,000
18B. Chrysene	BDL	2,000
19B. Dibenzo(a,h)Anthracene	BDL	2,000
20B. 1,2-Dichlorobenzene	BDL	2,000
21B. 1,3-Dichlorobenzene	BDL	2,000
22B. 1,4-Dichlorobenzene	BDL	2,000
23B. 3,3-Dichlorobenzidine	BDL	2,000
24B. Diethyl Phthalate	BDL	2,000
25B. Dimethyl Phthalate	BDL	2,000

BDL: Below Detection Limit

GC/MS FRACTION-BASE/NEUTRAL COMPOUNDS

Part II

Kemron Sample No.:

Sample Source:

COMPOUND	CONCENTRATION (UG/L)	DETECTION LIMIT (UG/L)
26B. Di-N-Butyl Phthalate	BDL	2,000
27B. 2,4-Dinitrotoluene	BDL	2,000
28B. 2,6-Dinitrotoluene	BDL	2,000
29B. Di-N-Octyl Phthalate	BDL	2,000
30B. 1,2-Diphenylhydrazine (as Azobenzene)	BDL	2,000
31B. Fluoranthene	BDL	2,000
32B. Fluorene	BDL	2,000
33B. Hexachlorobenzene	BDL	2,000
34B. Hexachlorobutadiene	BDL	2,000
35B. Hexachlorocyclopentadiene	BDL	2,000
36B. Hexachloroethane	BDL	2,000
37B. Indeno(1,2,3-cd)Pyrene	BDL	2,000
38B. Isophorone	BDL	2,000
39B. Naphthalene	BDL	2,000
40B. Nitrobenzene	16,000	2,000
41B. N-Nitrosodimethylamine	BDL	2,000
42B. N-Nitrosodi-N-Propylamine	BDL	2,000
43B. N-Nitrosodiphenylamine	BDL	2,000
44B. Phenanthrene	BDL	2,000
45B. Pyrene	BDL	2,000
46B. 1,2,4-Trichlorobenzene	BDL	2,000
47B. Aniline	BDL	2,000

BDL: Below Detection Limit

Date Extracted: 02/03/86 By: Sayi Malineni

Date Analyzed: 02/05/86 By: Seshu Chalasani

Time of Analysis:

Comments:

The sample was dark brown in color and exhibiting strong odor of organics. Only 50 ml of the sample was processed for extraction. The organic extract was again dark in color and was diluted to 10 ml. Accordingly, the detection limits are high.

QUALITY ASSURANCE SECTION
AND
ATTACHMENTS

- A. Surrogate Compound Recovery
- B. Mass Spectrum - BFB
- C. Mass List - BFB
- D. Method 624 (VOA) Blank RIC
- E. Method 624 (VOA) Standard RIC
- F. Method 624 (VOA) Sample RIC
- G. Mass Spectra - Identified VOA Compounds
- H. Mass Spectrum DFPTT
- I. Mass List DFPTT
- J. Method 625 (SV) Blank RIC
- K. Method 625 (SV) Standard RIC
- L. Method 625 (SV) Sample RIC
- M. Mass Spectra - Identified SV Compounds
- N. Chain-of-Custody Record
(if initiated by client)
- O. Glossary

PERCENT RECOVERY OF SURROGATES

FOR VOA & BNA

Sample Source:

Compound Name

1,2-Dichloroethane-d ₄ (VOA)	102
---	-----

Toluene-d ₈ (VOA)	86
------------------------------	----

4-Bromofluorobenzene (VOA)	100
----------------------------	-----

2-Fluorophenol (BNA)	Diluted Out
----------------------	-------------

Phenol d5 (BNA)	Diluted Out
-----------------	-------------

.trobenezene d5 (BNA)	Diluted Out
-----------------------	-------------

2-Fluorobiphenyl (BNA)	Diluted Out
------------------------	-------------

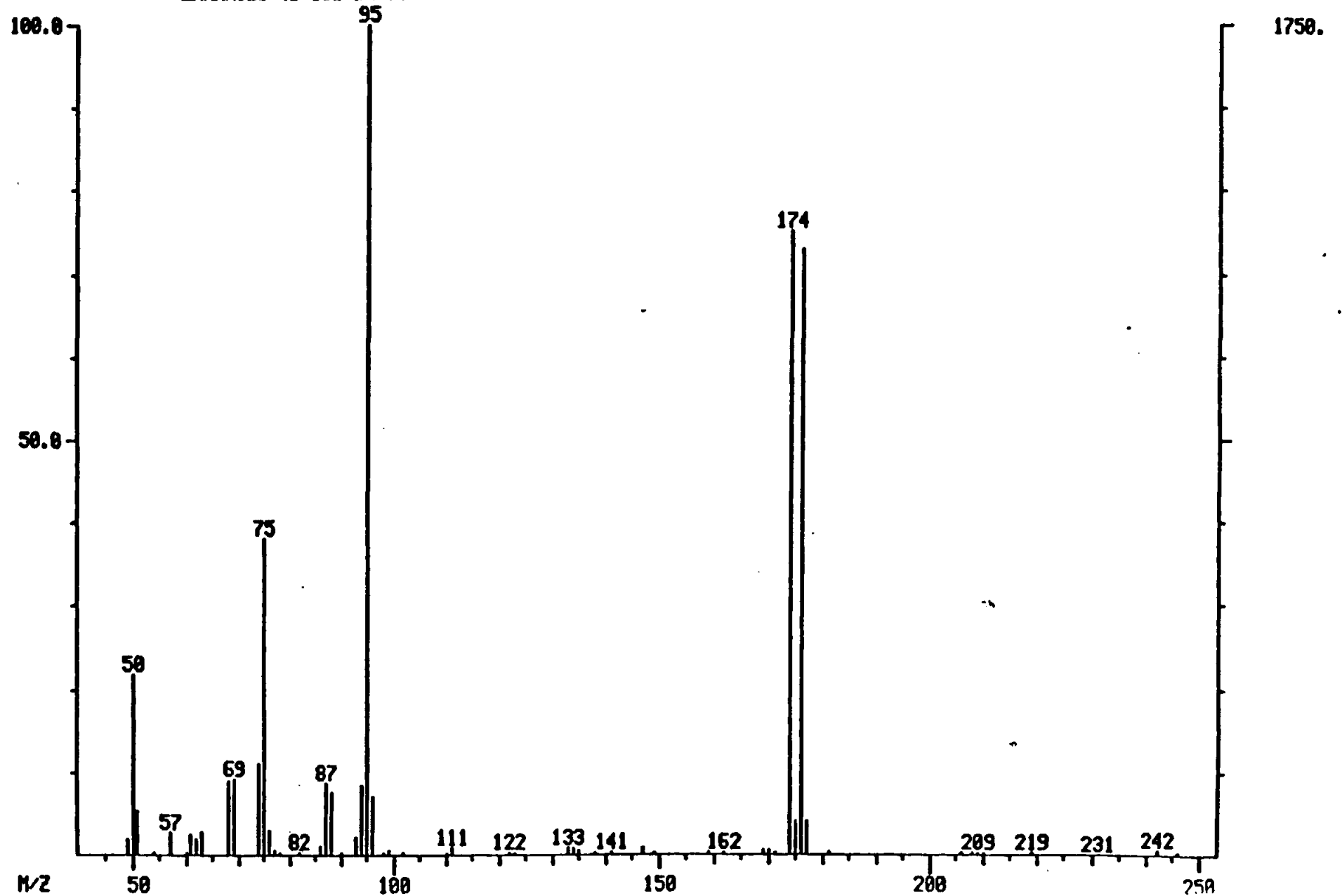
2,4,6-Tribromophenol (BNA)	Diluted Out
----------------------------	-------------

p-Tarphenyl d14 (BNA)	Diluted Out
-----------------------	-------------

MASS SPECTRUM
02/05/86 19:01:00 + 3:15
SAMPLE: 50NG BFB
CONDS.: ISOTHERMAL 0220C
ENHANCED (S 158 2N 0T)

DATA: BFB2586 #65
CALI: BFB2586 #3

BASE M/Z: 95
RIC: 7216.



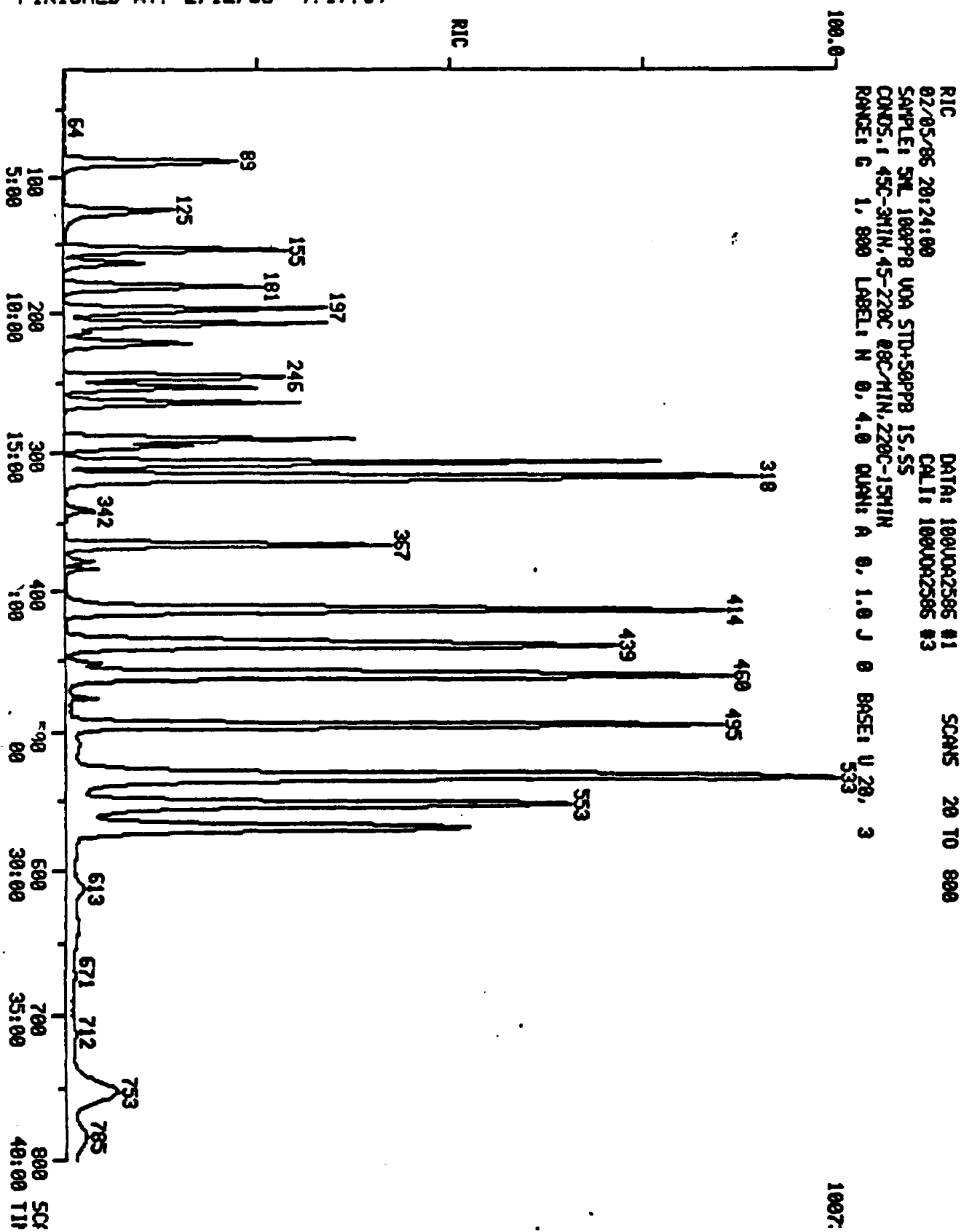
Mass List
02/05/86 19:01:00 + 3:15
Sample: 50NG BFB
Conds.: ISOTHERMAL e220C
Enhanced (S 158 2N OT)

Data: BFB2586 # 65
Call: BFB2586 # 3

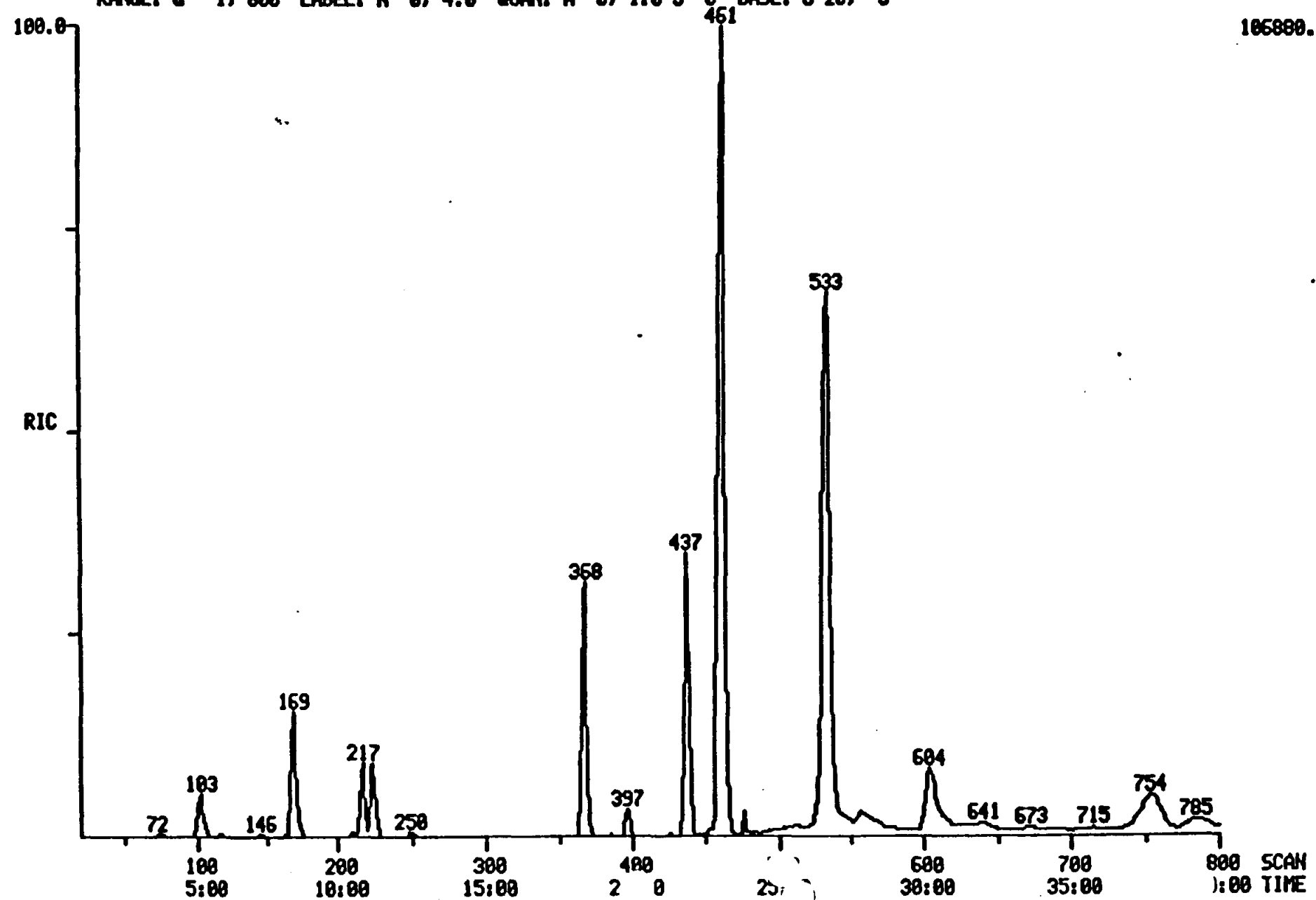
Base m/z: 95
RIC: 7216.

49 246 Mass	0.00		0.00		O. # Inten.	Minima O Maxima		Min Inten:		0.	
	% RA	% RIC	% RA	% RIC		Mass	% RA	% RIC	Inten.	% RA	% RIC
49.00	1.89	0.46			33.	169.00	0.57	0.14			
50.00	21.89	5.31			383.	170.00	0.63	0.15			10.
51.00	5.37	1.30			94.	171.00	0.40	0.10			11.
52.00	0.11	0.03			2.	174.00	74.97	18.18			7.
54.00	0.34	0.08			6.	175.00	4.00	0.97			1312.
57.00	2.63	0.64			46.	176.00	72.80	17.66			70.
60.00	0.29	0.07			5.	177.00	4.06	0.98			1274.
61.00	2.34	0.57			41.	181.00	0.17	0.04			71.
62.00	2.00	0.49			35.	206.00	0.17	0.04			3.
63.00	2.57	0.62			45.	208.00	0.23	0.06			4.
66.00	0.06	0.01			1.	209.00	0.40	0.10			7.
68.00	8.80	2.13			154.	210.00	0.23	0.06			4.
69.00	9.26	2.25			162.	219.00	0.17	0.04			3.
74.00	11.03	2.67			193.	231.00	0.11	0.03			2.
75.00	38.11	9.24			667.	234.00	0.11	0.03			2.
76.00	2.86	0.69			50.	242.00	0.51	0.12			9.
77.00	0.51	0.12			9.	243.00	0.11	0.03			2.
78.00	0.34	0.08			6.	246.00	0.17	0.04			3.
82.00	0.23	0.06			4.						
86.00	1.03	0.25			18.						
87.00	8.69	2.11			152.						
88.00	7.49	1.82			131.						
90.00	0.29	0.07			5.						
93.00	2.11	0.51			37.						
94.00	8.46	2.05			148.						
95.00	100.00	24.25			1750.						
96.00	6.91	1.68			121.						
98.00	0.34	0.08			6.						
99.00	0.63	0.15			11.						
100.00	0.11	0.03			2.						
102.00	0.17	0.04			3.						
110.00	0.23	0.06			4.						
111.00	0.80	0.19			14.						
112.00	0.11	0.03			2.						
114.00	0.11	0.03			2.						
122.00	0.29	0.07			5.						
123.00	0.23	0.06			4.						
133.00	0.91	0.22			16.						
134.00	0.69	0.17			12.						
135.00	0.57	0.14			10.						
138.00	0.17	0.04			3.						
139.00	0.11	0.03			2.						
141.00	0.29	0.07			5.						
147.00	0.80	0.19			14.						
148.00	0.11	0.03			2.						
149.00	0.40	0.10			7.						
150.00	0.11	0.03			2.						
159.00	0.17	0.04			3.						
161.00	0.06	0.01			1.						
162.00	0.34	0.08			6.						

TCA FINISHED, 7 FOUND
FINISHED AT: 2/12/86 9:17:59



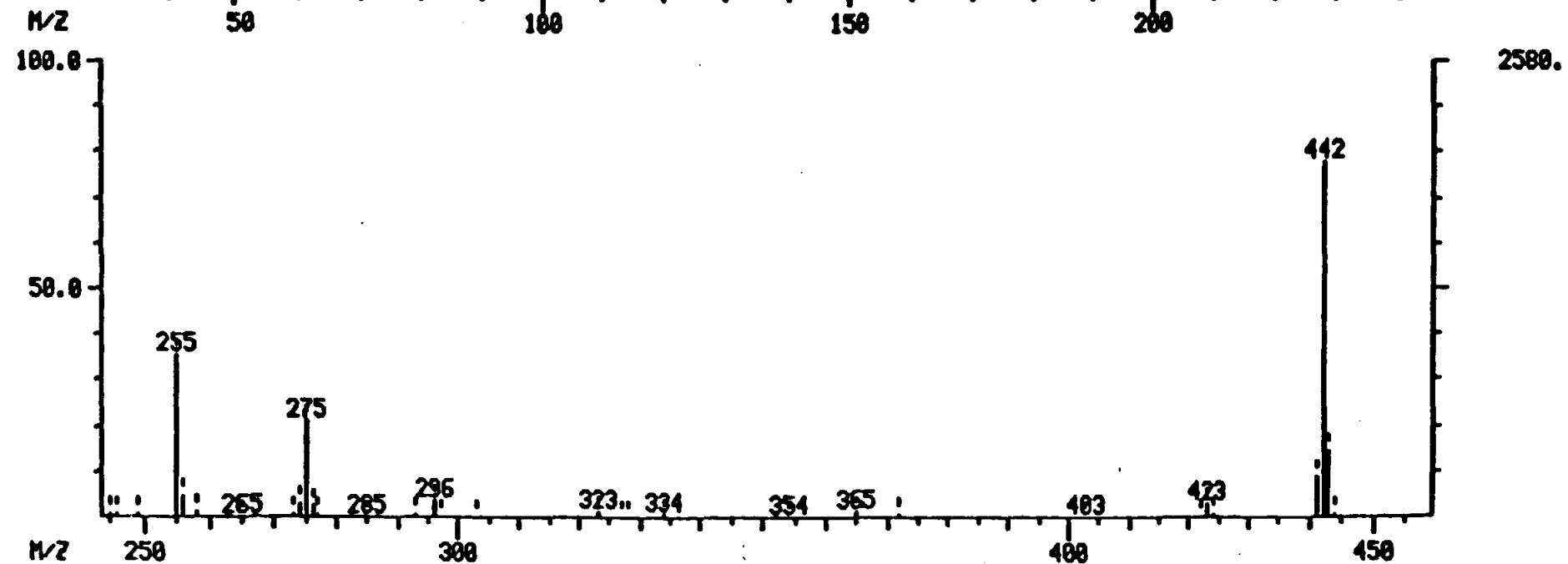
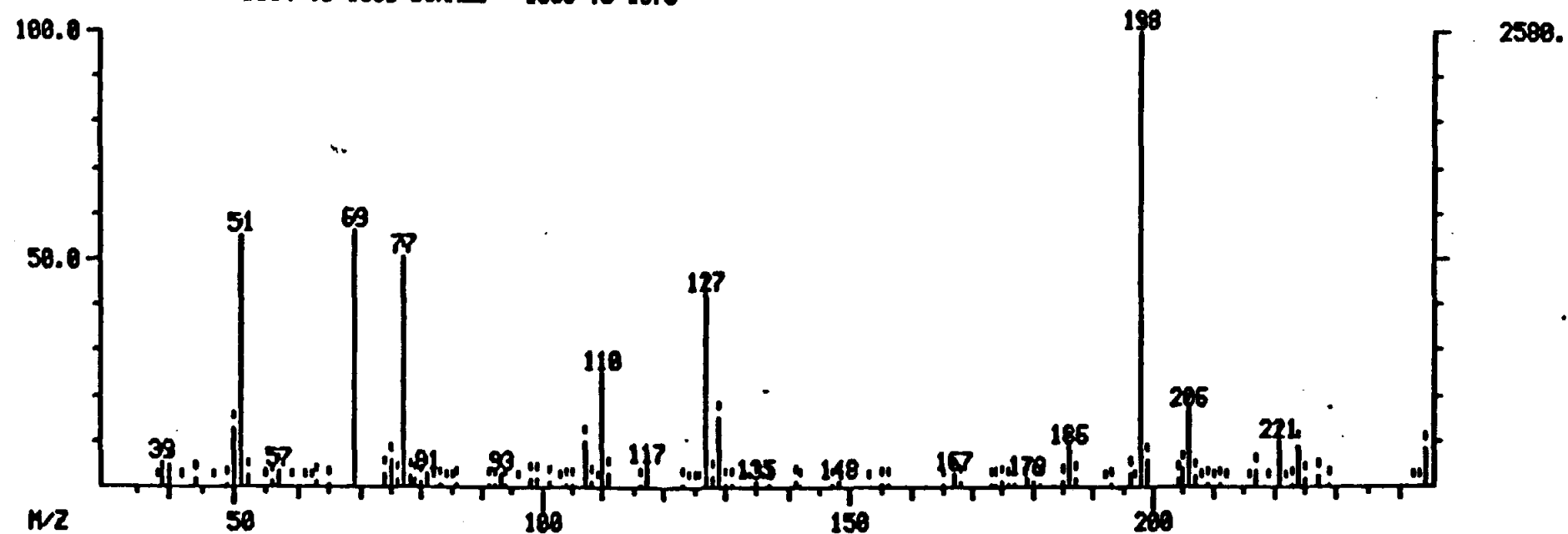
RIC
02/06/86 1:10:00
SAMPLE: UOA
COND.: 45C-3MIN, 45-220C @8C/MIN, 220C-15MIN
RANGE: G 1, 800 LABEL: N 0, 4.0 QUAN: A 0, 1.0 J 0 BASE: U 20, 3
DATA: UOA5610685 #1 SCANS 20 TO 800
CALI: UOA5610685 #3
100UL/SML+50PPB 15.55



MASS SPECTRUM
02/05/86 8:44:00 + 9:26
SAMPLE: 50NG DFTPP
COND.: 30C-4MIN, 30-310C 08C/MIN, 310C-10MIN
#564 TO #569 SUMMED - #558 TO #573

DATA: DF020586 #566
CALI: DF020586 #3

BASE M/Z: 198
RIC: 16528.

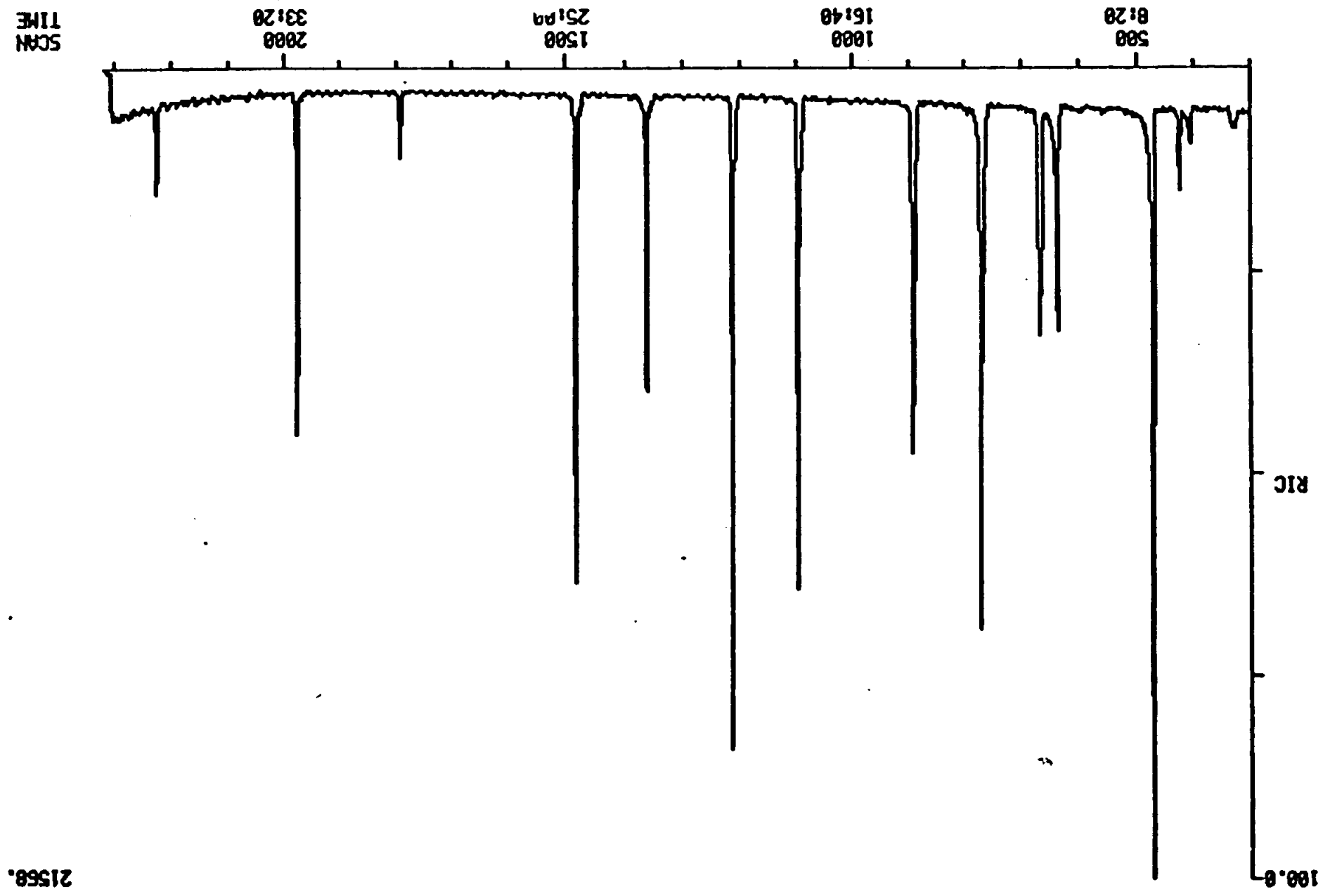


#564 to #569 summed - #558 to #573.

RIC: 18528.

38 444 Mass	0.00 % RA	0.00 % RIC	0.00 # 0 Inten.	Minima Maxima	Min Inten:	9.			
Mass	% RA	% RIC	Inten.	Mass	% RA	% RIC	Inten.		
39.007	S	5.12	0.71	132.	173.00	S	0.35	0.05	9.
40.00	S	4.77	0.66	123.	174.00	S	0.35	0.05	9.
44.00	S	1.51	0.21	39.	175.00	S	1.09	0.15	28.
49.00	S	0.50	0.07	13.	176.00	S	0.35	0.05	9.
50.00	S	12.64	1.76	326.	177.00	S	0.39	0.05	10.
51.00	S	55.27	7.70	1426.	179.00	S	1.59	0.22	41.
52.00	S	2.09	0.29	54.	180.00	S	1.01	0.14	26.
56.00	S	1.12	0.16	29.	181.00	S	0.47	0.06	12.
57.00	S	3.45	0.48	89.	185.00	S	0.89	0.12	23.
63.00	S	0.93	0.13	24.	186.00	S	8.60	1.20	222.
65.00	S	0.78	0.11	20.	187.00	S	1.98	0.28	51.
69.00	S	56.43	7.86	1456.	196.00	S	3.02	0.42	78.
74.00	S	3.06	0.43	79.	198.00	S	100.00	13.92	2580.
75.00	S	6.05	0.84	156.	199.00	S	5.74	0.80	148.
76.00	S	1.74	0.24	45.	204.00	S	1.59	0.22	41.
77.00	S	50.78	7.07	1310.	205.00	S	3.80	0.53	98.
78.00	S	2.36	0.33	61.	206.00	S	16.82	2.34	434.
79.00	S	1.98	0.28	51.	207.00	S	2.05	0.29	53.
80.00	S	1.20	0.17	31.	211.00	S	0.43	0.06	11.
81.00	S	2.64	0.37	68.	217.00	S	3.76	0.52	97.
83.00	S	0.47	0.06	12.	221.00	S	10.04	1.40	259.
86.00	S	0.78	0.11	20.	223.00	S	0.54	0.08	14.
91.00	S	0.35	0.05	9.	224.00	S	8.57	1.19	221.
92.00	S	0.43	0.06	11.	225.00	S	1.67	0.23	43.
93.00	S	3.06	0.43	79.	227.00	S	2.48	0.35	64.
94.00	S	0.39	0.05	10.	229.00	S	0.50	0.07	13.
98.00	S	1.74	0.24	45.	244.00	S	8.26	1.15	213.
99.00	S	1.59	0.22	41.	245.00	S	0.66	0.09	17.
101.00	S	1.12	0.16	29.	246.00	S	0.70	0.10	18.
104.00	S	0.54	0.08	14.	249.00	S	0.35	0.05	9.
105.00	S	0.43	0.06	11.	255.00	S	35.19	4.90	908.
107.00	S	9.65	1.34	249.	256.00	S	4.61	0.64	119.
108.00	S	1.32	0.18	34.	258.00	S	1.01	0.14	26.
110.00	S	25.12	3.50	648.	273.00	S	0.58	0.08	15.
111.00	S	3.06	0.43	79.	274.00	S	2.71	0.38	70.
117.00	S	4.57	0.64	118.	275.00	S	20.85	2.90	538.
123.00	S	0.54	0.08	14.	276.00	S	2.09	0.29	54.
127.00	S	42.25	5.88	1090.	277.00	S	0.54	0.08	14.
128.00	S	2.56	0.36	66.	293.00	S	0.39	0.05	10.
129.00	S	14.96	2.08	386.	296.00	S	3.22	0.45	83.
130.00	S	0.85	0.12	22.	323.00	S	1.40	0.19	36.
135.00	S	0.89	0.12	23.	334.00	S	0.50	0.07	13.
141.00	S	1.01	0.14	26.	365.00	S	1.43	0.20	37.
142.00	S	0.50	0.07	13.	372.00	S	0.54	0.08	14.
147.00	S	0.35	0.05	9.	423.00	S	3.02	0.42	78.
148.00	S	1.09	0.15	28.	424.00	S	0.39	0.05	10.
155.00	S	0.35	0.05	9.	441.00	S	8.95	1.25	231.
156.00	S	0.81	0.11	21.	442.00	S	77.67	10.82	2004.
167.00	S	2.64	0.37	68.	443.00	S	14.69	2.05	379.
168.00	S	1.36	0.19	35.	444.00	S	0.70	0.10	18.

RIC
02/05/86 9:08:00
DATA: SUBK2586 #470 SCANS 300 TO 2318
CALI: 505/2586 #3
SAMPLE: 1UL SU BLANK+40PPM IS+55
COND5: 30C-4MIN,30-310C 80C/MIN,310C-10MIN
RANGE: C 1,2318 LABEL: N 0, 4.0 QUAN: A 0, 1.0 J 0 BASE: U 20, 3
21568.

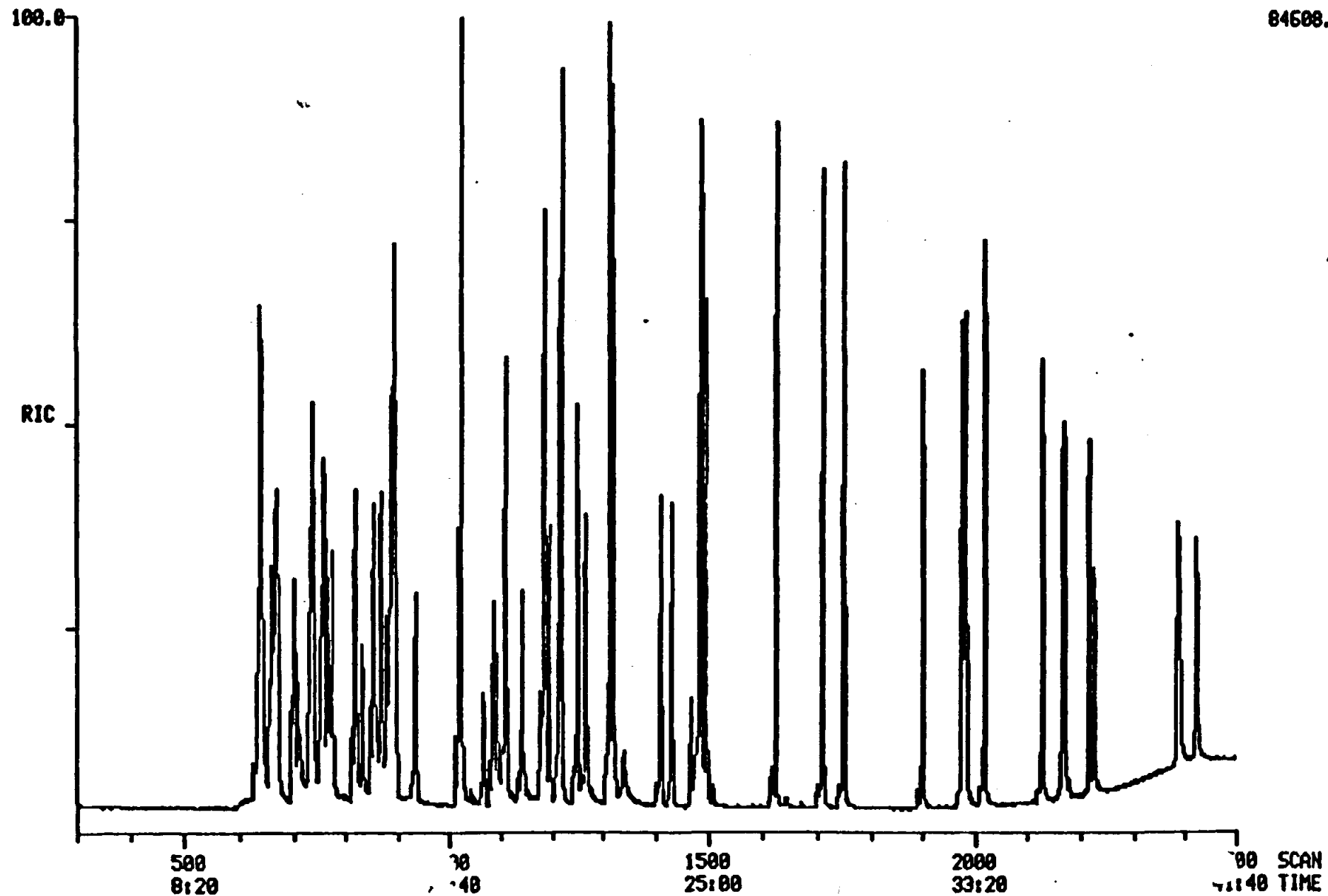


RIC
02/05/86 10:38:00
SAMPLE: 1UL SU 50PPM STD+40PPM 15
COND.: 30C-4MIN, 30-310C 0.8C/MIN, 310C-10MIN
RANGE: G 1,2500 LABEL: N 0, 4.0 QUAN: A 0, 1.0 J 0 BASE: U 20, 3

DATA: 50SU2506 01
CALI: 50SU2506 03

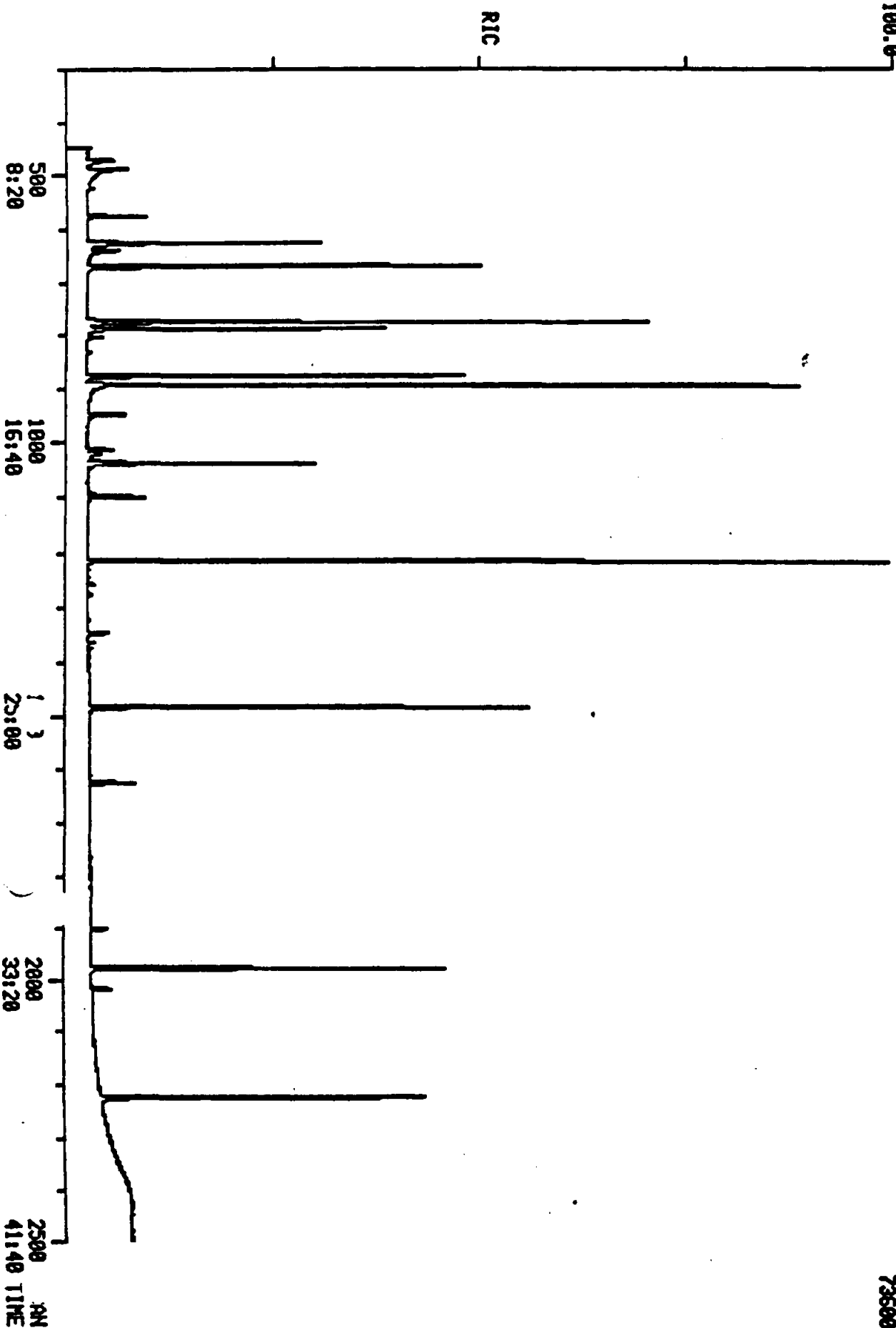
SCANS 300 TO 2500

84608.



RIC 02/05/86 16:23:00 DATA: SU5610685 #1 SCANS 300 TO 2500
SAMPLE: 1UL SUM CALL: SU5610559 #3
CONDS: 1 30C-4MIN, 30-310C 0.8C/MIN, 310C-10MIN SOL/10ML+40PPM 15+55
RANGE: C 1, 2500 LABEL: N 0, 4.0 Q/LAN: A 0, 1.0 J 0 BASE: U 20, 3

73600.



GLOSSARY

BFB:	Bromofluorobenzene; the compound specified in EPA Method 624 for which the mass spectrometer must meet performance criteria.
DFPTT:	Decafluorotriphenylphosphine; the compound specified in EPA Method 625 for which the mass spectrometer must meet performance criteria.
EPA Method 624:	standard method for determining volatile organic compounds in water using the purge and trap technique.
EPA Method 625:	standard for determining semivolatile organic compounds in water using liquid/liquid extraction.
IS:	Internal Standard; compound used to determine response factors (RF) for individual analytes and subsequent quantitative analysis.
RIC:	Reconstructed Ion Chromatograph; GC/MS chromatograph which plots total ion current versus scan number (time).
SS:	Surrogate Standard; quality control compounds similar to the compounds of interest which are spiked into every sample matrix. The surrogate's recovery is determined using the same internal standard procedures as the analytes.
SV:	semivolatile compounds; refers to the analytes determined by liquid/liquid extraction technique - Method 625.
VOA:	Volatile Organic Analysis; see EPA Method 624.

GERAGHTY & MILLER, INC.

Section No. 3.9
Revision No. 2
Date: 9-21-87
Page 3 of 3

**3.9.2 Contract Laboratory Program Statement of Work for
CompuChem Laboratories**

CONTRACT LABORATORY PROGRAM

STATEMENT OF WORK
(SOW)

INORGANIC ANALYSIS
Multi-Media
Multi-Concentration

SOW No. 786
October 1986 Rev.

Based on: Caucus Inorganics Protocol

STATEMENT OF WORK

TABLE OF CONTENTS

	Page
Preface: Scope of Work	Preface-1
Exhibit A: Summary of Requirements	A-1
Exhibit B: Reporting Requirements and Deliverables	B-1
1. Report Description	B-1
2. Contract Reporting Schedule & Distribution	B-5
3. Reporting Forms I-XIII	B-7
Exhibit C: Chemical Constituents to be Identified and Measured ...	C-1
Exhibit D: Analytical Methods	D-2
1. Sample Preparation - Water.....	D-2
2. Sample Preparation - Sediments, Soil and Sludges ..	D-3
Attachment 1: Acid Digestion of Sediments,	
Sludges and Soils	D-4
3. Analyses	D-7
ATTACHMENT 2: AAS-Furnace Methods	D-7
- 3: ICP Methods	D-20
- 4: AAS-Flame Methods	D-35
- 5: Mercury Analysis-Water (Manual) ...	D-39
- 5A: Mercury Analysis-Water (Automated).	D-46
- 6: Mercury Analysis-Sediments.....	D-53
- 7: Cyanide-Water.....	D-58
- 8: Cyanide-Solids.....	D-70
- 9: Percent Solids.....	D-82
- 10: Alternate Methods (Catastrophic)...	D-84
Exhibit E: Quality Assurance/Quality Control Requirements.....	E-1
General QA/QC Requirements.....	E-1
QA/QC Analytical Requirements.....	E-2
Lab Audit Procedures.....	E-17
Exhibit F: Sample Preservation and Holding Times.....	F-1
Exhibit G: Chain-of-Custody and Document Control Procedures.....	G-2

SCOPE OF WORK

The purpose of this contract is to provide EPA with chemical analytical services using inductively coupled plasma (ICP) emission spectroscopy, flame, flameless and cold vapor atomic absorption (AA) spectroscopy, and specified cyanide techniques for the analysis of field samples, the majority of which will be hazardous waste disposal site samples. These samples are expected to contain hazardous substances in concentrations ranging from parts per million to 15% of the total sample. When an analyte concentration exceeds the calibrated or linear range, reanalysis of the prepared sample after appropriate dilution is required.

Procedures specified herein shall be used in the preparation and analysis of aqueous and solid samples for the presence and quantitation of up to 23 indicated elements and cyanide. The Contractor shall employ safe handling procedures and generally accepted good laboratory practices in the performance of contract requirements and shall follow the quality assurance/quality control program specified herein.

The data obtained under this contract will be used by EPA to determine the existence and extent of threats to the public and the environment posed by hazardous waste disposal sites. The data may be used in civil and/or criminal litigation which requires the strictest adherence to chain-of-custody protocol, document control, and quality assurance procedures.

EXHIBIT A

SUMMARY OF REQUIREMENTS

General Requirements

The Contractor shall use proven instruments and approved techniques to prepare samples for analysis and to identify and measure the elements and inorganic species presented in Exhibit C.

The Contractor shall perform all analyses including necessary sample preparation procedures as prescribed in Exhibit D, while adhering to requirements for sample containers, preservation procedures and maximum holding times in Exhibit F.

The Contractor shall follow the designated quality assurance and quality control protocol (Exhibit E) and shall employ chain-of-custody and document control procedures in all aspects of sample handling and documentation as specified in Exhibit G.

Following sample analysis, the Contractor shall perform data reduction and shall report analytical activities, sample data, and quality control documentation as designated in Exhibit B.

This analytical activity using procedures specified in this SOW will identify and quantitate the parameters specified in Exhibit C in hazardous waste samples.

Specific Requirements

The Contractor shall provide the required analytical expertise and instrumentation for analyses of the listed elements and cyanide equal to or lower than the detection limits specified in Exhibit C. In Exhibit D, EPA provides the Contractor with the specific sample preparation techniques for aqueous solid samples and analytical procedures which must be used. A schematic flow chart depicting the complete low level-medium level inorganics analytical scheme is presented on page B-1.

The Contractor shall analyze samples within the maximum holding time specified in Exhibit F even if these times are less than the maximum 35-day completion time allowed in this contract.

Note: The Contractor is advised that the samples received under this contract are usually from known or suspected hazardous waste sites and may contain higher (greater than 15%) levels of organic and inorganic materials of a potentially hazardous nature and of unknown structure and concentration and should be handled throughout the analysis with appropriate caution. It is the contractor's responsibility to take all necessary measures to ensure laboratory safety.

For each sample received, the Contractor may be required to perform the analyses described in paragraphs 1, 2 and 3, following. (The documentation that accompanies the sample(s) to the Contractor facility shall indicate specific analytical requirements for that sample or set of samples, by task and/or by specific target parameters.)

- b. Sample shipments will be scheduled by groups of samples, each defined as a Case and identified by a unique SMO Case number. A Case signifies a group of samples collected at one site or geographical area over a predetermined time period, and will include one or more field samples with associated blanks. Samples may be shipped to the Contractor in a single shipment or multiple shipments over a period of time, depending on the size of the Case.
- c. Each sample received by the Contractor should be labeled with a SMO sample number, and accompanied by a Traffic Report form bearing the sample number and descriptive information regarding the sample. The Contractor shall complete and sign the Traffic Report, recording the date of sample receipt and sample condition on receipt for each sample container. The Contractor shall submit the signed copy of each Traffic Report to SMO within seven (7) calendar days following sample receipt (see contract delivery schedule). If there are problems either with the samples (e.g., mixed media, containers broken or leaking) or paperwork (e.g., Traffic Reports not with shipment, sample and Traffic Report numbers do not correspond) the Contractor shall immediately contact SMO for resolution.
- d. The SMO Case and sample numbers shall be used by the Contractor in identifying samples received under this contract both verbally and in reports/correspondence.
- e. Samples will routinely be shipped to the Contractor through an overnight delivery service. However, as necessary, the Contractor shall be responsible for any handling or processing required for the receipt of sample shipments, including pick-up of samples at the nearest servicing airport, bus station or other carrier service within the Contractor's geographical area. The Contractor shall be available to receive sample shipments at any time the delivery service is operating, including Saturdays.
- f. The Contractor shall accept all samples scheduled by SMO, provided that the total number of samples received in any calendar month does not exceed the monthly limitation expressed in the contract. Should the Contractor elect to accept additional samples, the Contractor shall remain bound by all contract requirements for analysis of those samples accepted.

5. Definition of a Sample

A sample consists of all components, perhaps more than one phase, contained inside appropriate receptacles. More than one container may be used for a single sample; individual containers may contain preservatives for different analysis portions. Containers may be glass or plastic.

- 6. The Contractor shall adhere to chain-of-custody and document control procedures described in Exhibit G. Documentation as described therein shall be required to show that all procedures are being strictly followed. This documentation must be reported for each sample as specified in Exhibit B. The data must be reported in the exact format of the EPA forms, specified in Exhibit B.

EXHIBIT B
REPORTING REQUIREMENTS AND DELIVERABLES

REPORTING REQUIREMENTS AND DELIVERABLES

The contractor shall provide reports and other deliverables specified hereunder. Specific reports are described below. The Contract Reporting Schedule which follows the report descriptions gives delivery schedule and report distribution information, including addresses for report designees. All reports to multiple addresses must be sent out concurrently by whatever method necessary to meet the contract required time limits. All reports must also be submitted in a legible form or resubmission will be required at no additional cost to the Agency. All copies must be single-sided.

Report Description

- A. Weekly Progress Reports - Tabulation of samples received, date of receipt, and a tabulation of problems encountered.
- B. Sample Traffic Report (Original Lab Copy for Return to SMO) - Copy of SMO Sample Traffic Report with lab receipt information and original Contractor signature.
- C. Sample Data Package - Data report package for analyses of each sample (including all required QA/QC-Exhibit E) must be complete before submission, must be consecutively paginated and shall include:
 - 1) Copies of completed SMO Sample Traffic Reports with receipt of information completed for all samples reported in data package.
 - 2) The cover page for the inorganic analysis data package (Exhibit B) including general comments, Statement of Work (SOW) Number, unique QC Report No., sample EPA cross reference numbers in alpha-numeric order, footnotes used in the data package, and the statement on use of ICP background and interelement corrections for the samples. The SOW number defines the Statement of Work used to obtain the reported values. The QC Report No. is a unique number assigned by the contractor to all Quality Control Data Reports generated in conjunction with and supportive of a particular set of sample analyses. It is intended that the presence of the Q.C. Report No. on the Cover Page and on Form I Data Sheets will establish linkage and traceability of the sample analytical data to the associated quality control data.
 - 3) Tabulated analytical results (identification and quantification) of specified chemical constituents (Exhibit C) using specified chemical procedures (Exhibit D), reported on Form I, validated and signed in original signature by the Laboratory Manager or an authorized designee. The quantitative values will be reported in units of micrograms per liter (ug/l) for aqueous samples and milligrams per kilogram (mg/kg) for solid samples. The results for solid samples will be reported on a dry weight basis, and percent solids will be reported on Form I. It is not required to determine or report percent solids on aqueous samples. Analytical results for all sample duplicates are to be reported on separate Form I's. Analytical values are to be reported in accordance with the following instructions using the appropriate

precision criteria specified for Furnace AA analysis in Exhibit E cannot be met, flag the reported value with an "M". If the GFAA analytical (post-digest) spike recovery is not within specified control limits, flag the data with the letter "W". Use "S" as a footnote symbol to indicate a value determined by Method of Standard Additions. If the correlation coefficient (r) for Method of Standard Additions is less than 0.995, flag the value with an "S +" symbol.

- Under the comments section on Form I provide a brief physical description of the sample using the following guidelines:

- a. water samples - coloration and clarity
- b. solid samples - coloration, texture, and artifacts

Recommended Descriptive Terms

Coloration: red, blue, yellow, green, orange, violet, white, colorless, brown, grey, black

Clarity: clear, cloudy, opaque

Texture: Fine (powdery), medium (sand), coarse (large crystals or rocks)

Also note any significant changes that occur during sample preparation (i.e., coloration shifts, emulsion formation).

- 4) Analytical results for samples and spikes, duplicates, standards, ICP Interference Check Samples, reagent blanks, laboratory control samples, and holding times on QA Forms II, III, IV, V, V-A, VI, VII, VIII, IX and X. Multiple forms require identification (i.e. Form II-A, Form II-B etc.) Summarize each full method of standard addition performed on Form VIII. Quarterly verification of instrument parameter forms for the applicable quarter (Forms XI-XIII). All QC results reported on the forms must be calculated from the values entered on the forms.
- 5) Legible photocopy of raw data (sequential measurement readout record) clearly labeled with EPA sample number and sufficient information to unequivocally identify:
 - a) calibration standards (including source and prep date).
 - b) calibration blanks and preparation blanks.
 - c) initial and continuing calibration verification standards and interference check samples, and ICP serial dilution samples.
 - d) diluted and undiluted samples (by EPA number) and all weights, dilutions and volumes used to obtain the reported values. If

Information shall include a key to abbreviations, with response units stated.

D. Results of Intercomparison/Performance Evaluation(PE) Sample Analyses

Tabulation of analytical results for Intercomparison/PE Sample analyses include all requirements specified in C above.

E. Complete Case File Purge

The Complete Case File Purge package must include all laboratory records received or generated for a specific case that have not been previously submitted to EPA as deliverable. These items include but are not limited to: sample tags, custody records, sample tracking records, analysts logbook pages, bench sheets, instrument readout records, computer print-outs, raw data summaries, instrument logbook pages (including instrument conditions), correspondence, and the document inventory.

Shipment of each Complete Case File Purge package by first class mail, overnight carrier, priority mail or equivalent is acceptable. Custody seals, which are provided by EPA, must be placed on shipping containers and a document inventory and transmittal letter included. The laboratory is not required to maintain any documents for a case after shipment; however, it is recommended that you maintain a copy of the document inventory and transmittal letter.

F. Quarterly Verification of Instrument Parameters

The Contractor must perform and report quarterly verification of instrument detection limits by methods specified in Exhibit E and report type and model # for each instrument used on this contract. For the ICP instrumentation and methods, the Contractor must also report quarterly: linearity range verification, interelement correction factors (including method of determination), wavelengths used and integration times. This information is reported using Forms XI, XII and XIII. Submissions of Quarterly Verification of Instrument Parameters must include the raw data used to determine those values reported.

CONTRACT REPORTING SCHEDULE

Report	No. Copies	Delivery Schedule*	SMO(1)	EMSL/ LV(2)	Region/ Client(3)	CEAT NEIC(4)
A. Weekly Progress Report	1	Weekly	X			
B. Sample Traffic Report	1	7 days from receipt of sample	X			
C. Sample Data Package	3	35 days from receipt of sample	X	X	X	
D. Results of Inter-comparison Study/ PE Sample Analysis	1	35 days from receipt of sample	X	X		
E. Compilation of Complete Case File Purge Package	1	7 days after data submission			-----N/A-----	
F. Complete Case File Purge Package	1	180 days after data submission or 7 days from receipt of written request by PO or SMO				X
G. Quarterly Verification of Instrument Parameters	2	Quarterly: 15th day of January, April, July, October	X	X		

*Schedule designated in calendar days.

REPORT DISTRIBUTION ADDRESSEES:

- (1) USEPA
Contract Laboratory Program
Sample Management Office (SMO)
P.O. Box 818
Alexandria, VA 22313

For overnight delivery service,
use street address:

300 N. Lee Street
Alexandria, VA 22314

- (2) USEPA
Environmental Monitoring
Systems Laboratory (EMSL/LV)
P.O. Box 15027
Las Vegas, NV 89114
ATTN: Data Audit Staff

For overnight delivery service,
use street address:

944 E. Harmon, Exec. Ctr. Rm. 226
Las Vegas, NV 89109
ATTN: Data Audit Staff

- (3) USEPA REGIONS:

The CLP Sample Management Office will provide the contractor with the list of addresses for distribution to the ten EPA Regions. SMO will provide the Contractor with updated Regional address/name lists as necessary throughout the period of the contract.

- (4) USEPA
NEIC Contract Evidence Audit Team
3000 Youngfield, Suite 285
Lakewood, CO 80215

U.S. EPA Contract Laboratory Program
Sample Management Office
P.O. Box 818 - Alexandria, VA 22313
703/557-2490 FTS: 8-557-2490

Date _____

COVER PAGE
INORGANIC ANALYSES DATA PACKAGE

Lab Name _____ Case No. _____

SOW No. _____ Q.C. Report No. _____

Sample Numbers

<u>EPA No.</u>	<u>Lab ID No.</u>	<u>EPA No.</u>	<u>Lab ID No.</u>
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____

Comments: _____

ICP interelement and background corrections applied? Yes _____ No _____.
If yes, corrections applied before _____ or after _____ generation of raw data.

Footnotes:

NR - Not required

Form I:

- Value - If the result is a value greater than or equal to the instrument detection limit but less than the contract-required detection limit, report the value in brackets (i.e., [10]). Indicate the analytical method used with P (for ICP), A (for Flame AA) or F (for Furnace AA).
- U - Indicates element was analyzed for but not detected. Report with the instrument detection limit value (e.g., 10U).
- E - Indicates a value estimated or not reported due to the presence of interference. Explanatory note included on cover page.
- S - Indicates value determined by Method of Standard Addition.
- N - Indicates matrix spike sample recovery is not within control limits.
- * - Indicates duplicate analysis is not within control limits.
- † - Indicates the correlation coefficient for method of standard addition is less than 0.995
- M - Indicates duplicate injection results exceeded control limits.
- W - Indicates GFAA spike sample recovery is not within control limits.

Indicate method used: P for ICP; A for Flame AA and F for Furnace.

Form I

U.S. EPA Contract Laboratory Program
Sample Management Office
P.O. Box 818 - Alexandria, VA 22313
703/557-2490 FTS: 8-557-2490

EPA Sample No.

Date _____

INORGANIC ANALYSIS DATA SHEET

Lab Name _____

Case No. _____

SOW No. _____

Lab Receipt Date _____

Lab Sample ID. No. _____

QC Report No. _____

Elements Identified and Measured

Concentration: Low _____ Medium _____
Matrix: Water _____ Soil _____ Sludge _____ Other _____
ug/L or mg/kg dry weight (Circle One)

1. Aluminum _____	13. Magnesium _____
2. Antimony _____	14. Manganese _____
3. Arsenic _____	15. Mercury _____
4. Barium _____	16. Nickel _____
5. Beryllium _____	17. Potassium _____
6. Cadmium _____	18. Selenium _____
7. Calcium _____	19. Silver _____
8. Chromium _____	20. Sodium _____
9. Cobalt _____	21. Thallium _____
10. Copper _____	22. Vanadium _____
11. Iron _____	23. Zinc _____
12. Lead _____	Percent Solids (%) _____
Cyanide _____	

Footnotes: For reporting results to EPA, standard result qualifiers are used as defined on Cover Page. Additional flags or footnotes explaining results are encouraged. Definition of such flags must be explicit and contained on Cover Page, however.

Comments: _____

Lab Manager _____

Form 11 (Part 1)

Q. C. Report No. _____

INITIAL AND CONTINUING CALIBRATION VERIFICATION³

Lab Name _____

Case No. _____

Date _____

SOW No. _____

Units : ug/L

Compound	Initial Calibration ¹			Continuing Calibration ²					
Metals:	True Value	Found	ZR	True Value	Found	ZR	Found	ZR	Method
1. Aluminum									
2. Antimony									
3. Arsenic									
4. Barium									
5. Beryllium									
6. Cadmium									
7. Calcium									
8. Chromium									
9. Cobalt									
10. Copper									
11. Iron									
12. Lead									
13. Magnesium									
14. Manganese									
15. Mercury									
16. Nickel									
17. Potassium									
18. Selenium									
19. Silver									
20. Sodium									
21. Thallium									
22. Vanadium									
23. Zinc									
Cyanide									
Other:									

¹ Initial Calibration Source _____

² Continuing Calibration Source _____

³ Control Limits: Mercury 80-120;

⁴ Indicate Analytical Method Used:

Other Metals 90-110; Cyanide 85-115

P - ICP; A - Flame AA; F - Furnace AA

Form II (Part 2)

Q. C. Report No. _____

LINEAR RANGE ANALYSIS AND CRDL STANDARD FOR AA³

Lab Name _____

Case No. _____

Date _____

SOW No. _____

Units : ug/L

Compound CRDL STD. For AA¹ Linear Range Analysis² (ICP)

Metals:	True Value	Found	ZR	True Value	Initial		Final	
					Found	ZR	Found	ZR
1. Aluminum								
2. Antimony								
3. Arsenic								
4. Barium								
5. Beryllium								
6. Cadmium								
7. Calcium								
8. Chromium								
9. Cobalt								
10. Copper								
11. Iron								
12. Lead								
13. Magnesium								
14. Manganese								
15. Nickel								
16. Potassium								
17. Selenium								
18. Silver								
19. Sodium								
20. Thallium								
21. Vanadium								
22. Zinc								
Other:								

¹ CRDL Standard Source _____

² Linear Range Standard Source _____

³ Linear Range Standard must be at 2x CRDL or 2x IDL whichever is higher

Form III

Q. C. Report No. _____

BLANKS

Lab Name _____

Case No. _____

Date _____

Units _____

Matrix _____

Compound	Initial Calibration Blank Value	<u>Continuing Calibration</u> <u>Blank Value</u>				<u>Preparation Blank¹</u> Matrix: Matrix:	
		1	2	3	4	1	2
Metals:							
1. Aluminum							
2. Antimony							
3. Arsenic							
4. Barium							
5. Beryllium							
6. Cadmium							
7. Calcium							
8. Chromium							
9. Cobalt							
10. Copper							
11. Iron							
12. Lead							
13. Magnesium							
14. Manganese							
15. Mercury							
16. Nickel							
17. Potassium							
18. Selenium							
19. Silver							
20. Sodium							
21. Thallium							
22. Vanadium							
23. Zinc							
Cyanide:							
Other:							

¹ Reporting units: aqueous, ug/L; solid, mg/kg

Form IV

Q. C. Report No. _____

ICP INTERFERENCE CHECK SAMPLE

Lab Name _____

Case No. _____

Date _____

Check Sample I.D. _____

ICP ID Code _____

Units: ug/L _____

Compound	True	Value ¹	Initial			Final		ZP
	Soln A ²	Soln AB ³	Soln A	Soln AB	ZR	Soln A	Soln AB	
Metals:								
1. Al								
2. Sb								
3. As								
4. Ba								
5. Be								
6. Cd								
7. Ca								
8. Cr								
9. Co								
10. Cu								
11. Fe								
12. Pb								
13. Mg								
14. Mn								
15. Hg								
16. Ni								
17. K								
18. Se								
19. Ag								
20. Na								
21. Tl								
22. V								
23. Zn								
Other:								

¹ True values of EPA ICP Interference Check Sample Set.

² Soln A is the Interference Metal Solution without the analyte solution added.

³ Soln AB is the combined Interference and Analyte solutions.

Form V (Part 1)

Q. C. Report No. _____

SPIKE SAMPLE RECOVERY

Lab Name _____

Case No. _____

Date _____

EPA Sample No. _____

Lab Sample ID No. _____

Units² _____

Matrix _____

Compound	Control Limit ZR	Spiked Sample Result (SSR)	Sample Result (SR)	Spike Added (SA)	ZR ¹
Metals:				F	
1. Aluminum	75-125				
2. Antimony	-				
3. Arsenic	-				
4. Barium	-				
5. Beryllium	-				
6. Cadmium	-				
7. Calcium	-				
8. Chromium	-				
9. Cobalt	-				
10. Copper	-				
11. Iron	-				
12. Lead	-				
13. Magnesium	-				
14. Manganese	-				
15. Mercury	-				
16. Nickel	-				
17. Potassium	-				
18. Selenium	-				
19. Silver	-				
20. Sodium	-				
21. Thallium	-				
22. Vanadium	-				
23. Zinc	-				
Cyanide:	-				
Other:					

¹ ZR = [(SSR - SR)/SA] x 100, ² Reporting Units: aqueous, ug/L; solid, mg/kg

N- out of control, NR - Not required

Comments: _____

Form V (Part 2)

QC Report No. _____

POST DIGEST SPIKE SAMPLE RECOVERY

Lab Name _____

Case No. _____

Date _____

EPA Sample No. _____

Lab Sample ID No. _____

Units¹ _____

Matrix _____

Compound	Spiked Sample Result (SSR)	Sample Result(SR)	Spike Added (SA)	ZR ²
Metals:				
1. Aluminum				
2. Antimony				
3. Arsenic				
4. Barium				
5. Beryllium				
6. Cadmium				
7. Calcium				
8. Chromium				
9. Cobalt				
10. Copper				
11. Iron				
12. Lead				
13. Magnesium				
14. Manganese				
15. Mercury				
16. Nickel				
17. Potassium				
16. Selenium				
19. Silver				
20. Sodium				
21. Thallium				
22. Vanadium				
23. Zinc				
Cyanide:				
Other:				

¹ Reporting Units: aqueous, ug/L, solid, mg/kg

² ZR = [(SSR - SR)/SA] x 100

NR - Not required

Comments: _____

Form VI

Q. C. Report No. _____

DUPLICATES

Lab Name _____

Case No. _____

Date _____

EPA Sample No. _____

Lab Sample ID No. _____

Units³ _____

Matrix _____

Compound	Control Limit ¹	Sample(S)	Duplicate(D)	RPD ²
Metals:				
1. Aluminum				
2. Antimony				
3. Arsenic				
4. Barium				
5. Beryllium				
6. Cadmium				
7. Calcium				
8. Chromium				
9. Cobalt				
10. Copper				
11. Iron				
12. Lead				
13. Magnesium				
14. Manganese				
15. Mercury				
16. Nickel				
17. Potassium				
18. Selenium				
19. Silver				
20. Sodium				
21. Thallium				
22. Vanadium				
23. Zinc				
Cyanide:				
XSolid				
Other:				

* Out of Control

¹ Refer to Exhibit E, $2 \text{ RPD} = [|S - D| / ((S + D)/2)] \times 100$

³ Reporting Units: aqueous, ug/L; solid, mg/kg

NC - Non calculable RPD due to value(s) less than CRDL

Form VII

Q.C. Report No. _____

LABORATORY CONTROL SAMPLE

Lab Name _____

Case No. _____

Date _____

SOLID LCS No. _____

AQUEOUS LCS No. _____

Compound	Laboratory Control Samples						
	Aqueous (ug/L)			Solid (mg/kg)			
	True	Found	ZR	True	Found	Limits	ZR
Metals:							
1. Aluminum							
2. Antimony							
3. Arsenic							
4. Barium							
5. Beryllium							
6. Cadmium							
7. Calcium							
8. Chromium							
9. Cobalt							
10. Copper							
11. Iron							
12. Lead							
13. Magnesium							
14. Manganese							
15. Mercury	NR	NR	NR				
16. Nickel							
17. Potassium							
18. Selenium							
19. Silver							
20. Sodium							
21. Thallium							
22. Vanadium							
23. Zinc							
Cyanide:							
Other:				NR	NR	NR	NR

NR - Not required

Q.C. Report No. _____

STANDARD ADDITION RESULTS

Case No. _____
Units: ug/L

1 Matrix abbreviations: Low Solid, LS; Medium Solid, MS; Low Aqueous, LA; Medium Aqueous, MA.
2 CON is the concentration added, ABS. is the instrument readout in absorbance or concentration.
3 Concentration as determined by MSA
*"r" is the correlation coefficient.
+ - Correlation coefficient is outside of control window of 0.995.

Form IX

Q. C. Report No. _____

ICP SERIAL DILUTIONS

Lab Name _____

Case No. _____

Date _____

EPA Sample No. _____

Lab Sample ID No. _____

Units: ug/L

Matrix _____

Compound	Initial Sample Concentration(I)	Serial Dilution ¹ Result(S)	% Difference ²
Metals:			
1. <u>Aluminum</u>			
2. <u>Antimony</u>			
3. <u>Arsenic</u>			
4. <u>Barium</u>			
5. <u>Beryllium</u>			
6. <u>Cadmium</u>			
7. <u>Calcium</u>			
8. <u>Chromium</u>			
9. <u>Cobalt</u>			
10. <u>Copper</u>			
11. <u>Iron</u>			
12. <u>Lead</u>			
13. <u>Magnesium</u>			
14. <u>Manganese</u>			
15. <u>Nickel</u>			
16. <u>Potassium</u>			
17. <u>Selenium</u>			
18. <u>Silver</u>			
19. <u>Sodium</u>			
20. <u>Thallium</u>			
21. <u>Vanadium</u>			
22. <u>Zinc</u>			
Other:			

¹ Diluted sample concentration corrected for 1:4 dilution (see Exhibits D,E)

² Percent Difference = $\frac{|I - S|}{I} \times 100$

NR - Not Required, initial sample concentration less than 10 times IDL after dilution.

NA - Not Applicable, analyte not determined by ICP

Form XI

INSTRUMENT DETECTION LIMITS (Quarterly)

LAB NAME _____ DATE _____

ICP/Flame AA (Circle One) Model Number _____ Furnace AA Number _____

Element	Wavelength (nm)	CRDL (ug/L)	IDL (ug/L)	Element	Wavelength (nm)	CRDL (ug/L)	IDL (ug/L)
1. Aluminum		200		13. Magnesium		5000	
2. Antimony		60		14. Manganese		15	
3. Arsenic		10		15. Mercury		0.2	
4. Barium		200		16. Nickel		40	
5. Beryllium		5		17. Potassium		5000	
6. Cadmium		5		18. Selenium		5	
7. Calcium		5000		19. Silver		10	
8. Chromium		10		20. Sodium		5000	
9. Cobalt		50		21. Thallium		10	
10. Copper		25		22. Vanadium		50	
11. Iron		100		23. Zinc		20	
12. Lead		5					

Footnotes: o Indicate the instrument for which the IDL applies with a "P" (for ICP), an "A" (for Flame AA), or an "F" (for Furnace AA) behind the IDL value.

o Indicate elements commonly run with background correction (AA) with a "B" behind the analytical wavelength.

o If more than one ICP/Flame or Furnace AA is used, submit separate Forms XI-XIII for each instrument.

COMMENTS: _____

Lab Manager _____

Form XII (Part 1)

ICP INTERELEMENT CORRECTION FACTORS (Quarterly)

LABORATORY _____ ICP Model Number _____

DATE _____

Analyte	Analyte Wavelength (nm)	Interelement Correction Factors for							
		Al	Ca	Fe	Mg				
1. <u>Antimony</u>									
2. <u>Arsenic</u>									
3. <u>Barium</u>									
4. <u>Beryllium</u>									
5. <u>Cadmium</u>									
6. <u>Chromium</u>									
7. <u>Cobalt</u>									
8. <u>Copper</u>									
9. <u>Lead</u>									
10. <u>Manganese</u>									
11. <u>Mercury</u>									
12. <u>Nickel</u>									
13. <u>Potassium</u>									
14. <u>Selenium</u>									
15. <u>Silver</u>									
16. <u>Sodium</u>									
17. <u>Thallium</u>									
18. <u>Vanadium</u>									
19. <u>Zinc</u>									

COMMENTS: _____

Lab Manager _____

Form X11 (Part 2)

ICP INTERELEMENT CORRECTION FACTORS (Quarterly)

LABORATORY _____ ICP Model Number _____

DATE _____

		Interelement Correction Factors for							
Analyte	Analyte Wavelength (nm)					f			
1. <u>Antimony</u>									
2. <u>Arsenic</u>									
3. <u>Barium</u>									
4. <u>Beryllium</u>									
5. <u>Cadmium</u>									
6. <u>Chromium</u>									
7. <u>Cobalt</u>									
8. <u>Copper</u>									
9. <u>Lead</u>									
10. <u>Manganese</u>									
11. <u>Mercury</u>									
12. <u>Nickel</u>									
13. <u>Potassium</u>									
14. <u>Selenium</u>									
15. <u>Silver</u>									
16. <u>Sodium</u>									
17. <u>Thallium</u>									
18. <u>Vanadium</u>									
19. <u>Zinc</u>									

COMMENTS: _____

Lab Manager _____

Form XIII

ICP LINEAR RANGES (Quarterly)

LAB NAME _____ ICP Model Number _____
 DATE _____

Analyte	Integration Time (Seconds)	Concentration (ug/L)	Analyte	Integration Time (Seconds)	Concentration (ug/L)
1. Aluminum			13. Magnesium	f	
2. Antimony			14. Manganese		
3. Arsenic			15. Mercury		
4. Barium			16. Nickel		
5. Beryllium			17. Potassium		
6. Cadmium			18. Selenium		
7. Calcium			19. Silver		
8. Chromium			20. Sodium		
9. Cobalt			21. Thallium		
10. Copper			22. Vanadium		
11. Iron			23. Zinc		
12. Lead					

Footnotes: o Indicate elements not analyzed by ICP with the notation "NA".

COMMENTS: _____

Lab Manager _____

EXHIBIT C

CHEMICAL CONSTITUENTS TO BE IDENTIFIED AND MEASURED

Table 3 Elements Determined by Inductively Coupled
Plasma Emission or Atomic Absorption Spectroscopy

Element	Contract Required Detection Level (1,2) (ug/L)
Aluminum	200
Antimony	60
Arsenic	10
Barium	200
Beryllium	5
Cadmium	5
Calcium	5000
Chromium	10
Cobalt	50
Copper	25
Iron	100
Lead	5
Magnesium	5000
Manganese	15
Mercury	0.2
Nickel	40
Potassium	5000
Selenium	5
Silver	10
Sodium	5000
Thallium	10
Vanadium	50
Zinc	20

Table 2. Cyanide Determination

Element	Contract Required Detection Level (1, 2) ^c (ug/L)
Cyanide	10

- 1: Subject to the restrictions on page D-83, any analytical method specified in SOW Exhibit D may be utilized as long as the documented instrument or method detection limits meet the Contract Required Detection Level (CRDL) requirements. Higher detection levels may only be used in the following circumstance:

If the sample concentration exceeds five times the detection limit of the instrument or method in use, the value may be reported even though the instrument or method detection limit may not equal the contract required detection level. This is illustrated in the example below:

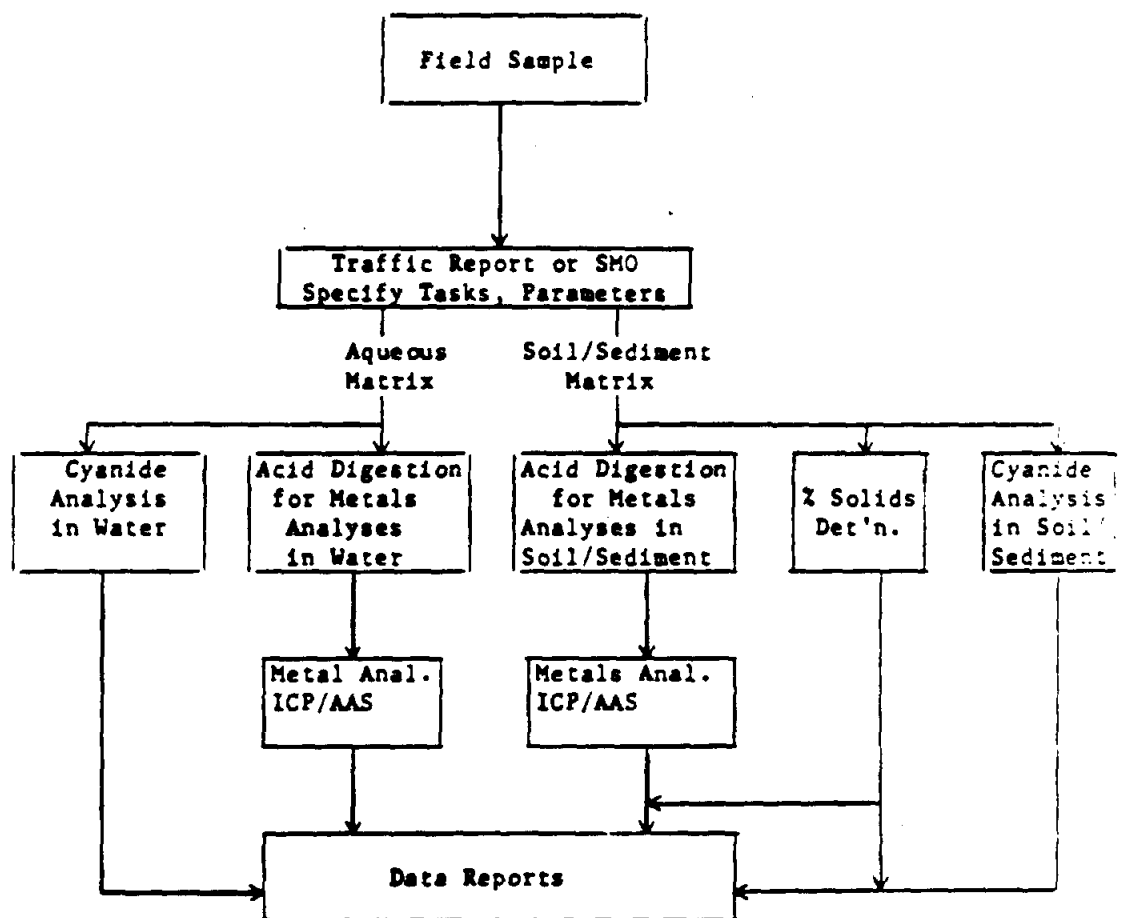
For lead:
 Method in use = ICP
 Instrument Detection Limit (IDL) = 40
 Sample concentration = 220
 Contract Required Detection Level (CRDL) = 5

The value of 220 may be reported even though instrument detection limit is greater than required detection level. The instrument or method detection limit must be documented as described in Exhibit E.

- 2: These CRDL are the instrument detection limits obtained in pure water that must be met using the procedure in Exhibit E. The detection limits for samples may be considerably higher depending on the sample matrix.

EXHIBIT D
ANALYTICAL METHODS

INORGANIC METHODS FLOW CHART



Analytical Methods

Subject to the restrictions on page D-83, any analytical method specified in Exhibit D may be utilized as long as the documented instrument or method detection limits meet the contract required detection levels (Exhibit C). Analytical methods with higher detection limits may be used only if the sample concentration exceeds five times the documented detection limit of the instrument or method. When an analyte concentration exceeds the calibrated or linear range, reanalysis of the prepared sample is required after appropriate dilution. All samples must initially be run undiluted (i.e. final product of sample preparation procedures). Unless contractor can submit proof that dilution was required to attain valid results, both diluted and undiluted sample measurements must be contained in the raw data. For sample dilution, the contractor must use the lowest dilution factor necessary to bring each analyte within the valid analytical range and report the highest valid value for each analyte.

Labware must be acid cleaned according to EPA's manual "Methods for Chemical Analysis of Water and Wastes" (Ref. 2) or an equivalent procedure. Samples must be opened and digested in a hood. Stock solutions for standards may be purchased or made up as specified in the analytical methods. Deionized water (Type II) is equivalent to distilled water. All sample dilutions should be made with acidified water to maintain constant acid strength. Background corrections are required for flame AA measurements below 350 nm and all furnace AA measurements. Before water sample preparation is initiated, check the pH of all water samples and note in the sample preparation log if it is less than 2 for metals and greater than 12 for cyanide.

For the analysis of samples for dissolved metals, SMO may specify that acid digestion not be performed and therefore sample preparation is not required, however, duplicates and matrix spikes are required. In this case the lab proceeds directly to sample analysis and no preparation blank or LCS is required for these samples.

Unless otherwise instructed by EPA, all samples must be mixed thoroughly prior to aliquoting for digestion.

1. Furnace AA/ICP/Flame AA - Water

Furnace Atomic Absorption

A. Sample Preparation (Furnace Digestion Procedure for Waters)

Shake sample and transfer 100 mL of well-mixed sample to a 250 mL beaker, add 1 mL of (1+1) HNO_3 and 2 mL 30% H_2O_2 . Cover with watch glass or similar cover, heat for 2 hours at 95°C or until the volume is reduced to between 25 and 50 mL (make certain samples do not boil). Cool sample and filter (see Note 1) to remove insoluble material and bring back to 100 mL with deionized distilled water. The sample is now ready for analysis.

Concentrations so determined shall be reported as "total".

If Sb is to be determined by furnace, use the digestates prepared for ICP/AA analysis.

B. Analytical Procedures

See Attachment 2 (Ref.3).

Each furnace analysis requires at least 2 burns, except when performing full method of standard additions (MSA).

Inductively Coupled Plasma (ICP) and Flame Atomic Absorption (AA)

A. Sample Preparation (ICP/Flame AA Digestion Procedure for Water)

Shake sample and transfer 100 mL of a well mixed sample to a beaker. Add 2 mL of (1+1) HNO₃ and 10 mL of (1+1) HCl to the sample. Cover with watch glass or similar cover and heat on a steam bath or hot plate until the volume has been reduced to between 25 and 50 mL making certain the sample does not boil. After this treatment, cool sample and filter to remove insoluble material that could clog the nebulizer. (See Note below.) Adjust the volume to 100 mL with deionized distilled water. The sample is now ready for analysis.

Concentrations so determined shall be reported as "total."

NOTE: In place of filtering, the sample after dilution and mixing may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

B. Analytical Procedures

ICP - See Attachment 3 (Ref. 4). Flame AA - See Attachment 4 (Ref. 5).

2. Furnace AA/ICP/Flame AA - Sediment, Sludges and Soils

A. Sample Preparation - Acid Digestion of Sediments, Sludges and Soils

See Attachment 1 (Ref. 6).

B. Analytical Procedures

Furnace AA - See Attachment 2.

Each furnace analysis requires at least 2 burns, except for full MSA.

ICP - See Attachment 3.

Flame AA - See Attachment 4.

3. Mercury in Water

See Attachment 5 (manual) and 5A (automated) (Ref. 7).

4. Mercury in Sediment

See Attachment 6 (Ref. 8).

6. Cyanide in Sediment

See Attachment 8 (Ref. 9).

5. Cyanide in Water

See Attachment 7 (Ref. 9).

7. Determination of Percent Solids

See Attachment 9.

Bibliography

1. Interim Methods for the Sampling and Analysis of Priority Pollutants in Sediments and Fish Tissue, USEPA Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, August 1977, Revised October 1980.
2. Methods for Chemical Analyses of Water and Wastes (EPA-600/4-79-020), Metals -4.
3. Ibid, Methods 204.2 (Sb), 206.2 (As), 210.2 (Be), 213.2 (Cd), 218.2⁶ (Cr), 239.2 (Pb), 270.2 (Se), 272.2 (Ag) and 279.2 (Tl).
4. "Inductively Coupled Plasma-Atomic Emission Spectrometric Method of Trace Elements Analysis of Water and Waste", Method 200.7 modified by CLP Inorganic Data/Protocol Review Committee; original method by Theodore D. Martin, EMSL/Cincinnati.
5. Op. Cit. (#2), Methods 215.1 (Ca), 242.1 (mg), 258.1 (K), 273.1 (Na).
6. Modification (by committee) of Method 3050, SW-846, 2nd ed., Test Methods for Evaluating Solid Waste, EPA Office of Solid Waste and Emergency Response, July 1982.
7. Op. Cit. (#2), Methods 245.1 or 245.2.
8. Op. Cit. (#2), Methods 245.5 modified (by committee).
9. Op. Cit. (#2), Methods 335.2 modified (by committee).

ATTACHMENT 1

SAMPLE PREPARATION OF SEDIMENTS, SLUDGES AND SOILS

1. Scope and Application

- 1.1 This method is an acid digestion procedure used to prepare sediments, sludges, and soil samples for analysis by flame or furnace atomic absorption spectroscopy (AAS) or by inductively coupled argon plasma spectroscopy (ICP). Samples prepared by this method may be analyzed by AAS or ICP for the following metals:

Aluminum	Chromium	Potassium
Antimony	Cobalt	Selenium
Arsenic	Copper	Silver
Barium	Iron	Sodium
Beryllium	Lead	Thallium
Cadmium	Magnesium	Vanadium
Calcium	Manganese	Zinc
	Nickel	

2. Summary of Method

- 2.1 A representative 1 g (wet weight) sample is digested in nitric acid and hydrogen peroxide. The digestate is then refluxed with either nitric acid or hydrochloric acid. Hydrochloric acid is used as the final reflux acid for the furnace AA analysis of Sb, the flame AA or ICP analysis of Al, Sb, Ba, Be, Ca, Cd, Cr, Co, Cu, Fe, Pb, Mg, Mn, Ni, K, Ag, Na, Tl, V and Zn. Nitric acid is employed as the final reflux acid for the furnace AA analysis of As, Be, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni, Se, Ag, Tl, V, and Zn. A separate sample shall be dried for a total solids determination (Exhibit D, Attachment 9).

3. Apparatus and Materials

- 3.1 250 ml beaker or other appropriate vessel
3.2 Watch glasses
3.3 Thermometer that covers range of 0° to 200°C
3.4 Whatman No. 42 filter paper or equivalent

4. Reagents

- 4.1 ASTM Type II water (ASTM D1193): Water must be monitored.
4.2 Concentrated Nitric Acid (sp. gr. 1.41)
4.3 Concentrated Hydrochloric Acid (sp. gr. 1.19)
4.4 Hydrogen Peroxide (30%)

5. Sample Preservation, and Handling

5.1 Non-aqueous samples must be refrigerated upon receipt until analysis.

6. Procedure

- 6.1 Mix the sample thoroughly to achieve homogeneity. For each digestion procedure, weigh (to the nearest 0.01gms) a 1.0 to 1.5 gm portion of sample and transfer to a beaker.
- 6.2 Add 10 ml of 1:1 nitric acid (HNO_3), mix the slurry, and cover with a watch glass. Heat the sample to 95°C and reflux for 10 minutes without boiling. Allow the sample to cool, add 5 ml of concentrated HNO_3 , replace the watch glass, and reflux for 30 minutes. Do not allow the volume to be reduced to less than 5 ml while maintaining a covering of solution over the bottom of the beaker.
- 6.3 After the second reflux step has been completed and the sample has cooled, add 2 ml of Type II water and 3 ml of 30% hydrogen peroxide (H_2O_2). Return the beaker to the hot plate for warming to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence. Heat until effervescence subsides, and cool the beaker.
- 6.4 Continue to add 30% H_2O_2 in 1 ml aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged. (NOTE: Do not add more than a total of 10 ml 30% H_2O_2 .)
- 6.5 If the sample is being prepared for the furnace AA analysis of Sb, the flame AA or ICP analysis of Al, Sb, Ba, Be, Ca, Cd, Cr, Co, Cu, Fe, Pb, Mg, Mn, Ni, K, Ag, Na, Tl, V, and Zn, add 5 ml of 1:1 HCl and 10 ml of Type II water, return the covered beaker to the hot plate, and heat for an additional 10 minutes. After cooling, filter through Whatman No. 42 filter paper (or equivalent) and dilute to 100 ml with Type II water (or centrifuge the sample - see Note 1). The diluted sample has an approximate acid concentration of 2.5% (v/v) HCl and 5% (v/v) HNO_3 . Dilute the digestate 1:1 (200 ml final volume) with acidified water to maintain constant acid strength. The sample is now ready for analysis.
- 6.6 If the sample is being prepared for the furnace analysis of As, Be, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni, Se, Ag, Tl, V, and Zn, continue heating the acid-peroxide digestate until the volume has been reduced to approximately 2 ml, add 10 ml of Type II water, and warm the mixture. After cooling, filter through Whatman No. 42 filter paper (or equivalent - see Note 1) and dilute to 100 ml with Type II water (or centrifuge the sample). The diluted digestate solution contains approximately 2% (v/v) HNO_3 . Dilute the digestate 1:1 (200 ml final volume) with acidified water to maintain constant acid strength. For analysis, withdraw aliquots of appropriate volume, and add any required reagent or matrix modifier. The sample is now ready for analysis.

NOTE 1: In place of filtering, the sample after dilution and mixing may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

7. Calculations

7.1 A separate determination of percent solids must be performed (Exhibit D, Attachment 9).

7.2 The concentrations determined in the digest are to be reported on the basis of the dry weight of the sample.

$$\text{Concentration (dry wt.) (mg/kg)} = \frac{C \times V}{W \times S}$$

where C = Concentration (mg/L)
V = Final volume in liters after sample preparation
W = Weight in kg of wet sample
S = % Solids/100

REF: Modification of Method 3050 from SW-846, Test Methods for Evaluating Solid Waste, EPA Office of Solid Waste and Emergency Response, July 1982.

8. Bibliography

1. Modification (by committee) of Method 3050, SW-846, 2nd ed., Test Methods for Evaluating Solid Waste, EPA Office of Solid Waste and Emergency Response, July 1982.

ATTACHMENT 2

ANTIMONY

Method 304.2 CLP-M (Atomic Absorption, furnace technique)

Optimum Concentration Range: 20-300 ug/l

Approximate Detection Limit: 3 ug/l

Preparation of Standard Solution

1. Stock solution: Carefully weigh 2.7426 g of antimony potassium tartrate (analytical reagent grade) and dissolve in deionized distilled water. Dilute to 1 liter with deionized water.
1 mL = 1 mg Sb (1000 mg/L).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".
3. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec-125°C.
2. Ashing Time and Temp: 30 sec-800°C.
3. Atomizing Time and Temp: 10 sec-2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 217.6 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer MGA-2100, based on the use of a 20 ul injection, continuous flow purge gas and pyrolytic graphite and are to be used as guidelines only. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is required.
3. Nitrogen may also be used as the purge gas.
4. If chloride concentration presents a matrix problem or causes a loss previous to atomization, add an excess 5 mg of ammonium nitrate to the furnace and ash using a ramp accessory or with incremental steps until the recommended ashing temperature is reached.

5. For every sample analyzed, verification is necessary to determine that method of standard addition is not required (see Exhibit E).
6. If method of standard addition is required follow the procedure given in Exhibit E.

ARSENIC

Method 206.2 CLP-M (Atomic Absorption, furnace technique)

Optimum Concentration Range: 5-100 ug/l

Approximate Detection Limit: 1 ug/l

Preparation of Standard Solution

1. Stock solution: Dissolve 1.320 g of arsenic trioxide, As_2O_3 (analytical reagent grade) in 100 ml of deionized distilled water containing 4 g NaOH. Acidify the solution with 20 ml conc. HNO_3 and dilute to 1 liter. 1 ml = 1 ug As (1000 ug/l).
2. Nickel Nitrate Solution, 5%: Dissolve 24.780 g of ACS reagent grade $Ni(NO_3)_2 \cdot 6H_2O$ in deionized distilled water and make up to 100 ml.
3. Nickel Nitrate Solution, 1%: Dilute 20 ml of the 5% nickel nitrate to 100 ml with deionized distilled water.
4. Working Arsenic Solution: Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. Withdraw appropriate aliquots of the stock solution, add 1 ml of conc. HNO_3 , 2 ml of 30% H_2O_2 and 2 ml of the 5% nickel nitrate solution. Dilute to 100 ml with deionized distilled water.

Sample Preparation

1. Add 100 ul of the 5% nickel nitrate solution to 5 ml of the digested sample. The sample is now ready for injection into the furnace.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec-125°C.
2. Ashing Time and Temp: 30 sec-1100°C.
3. Atomizing Time and Temp: 10 sec-2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 193.7 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer MGA-2100, based on the use of a 20 ul injection, purge gas interrupt and non-pyrolytic graphite. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is required. Background correction made by the deuterium arc method does not adequately compensate for high levels of certain interferences (ie., Al, Fe). If conditions occur where significant interference is suspected, the lab must switch to an alternate wavelength or take other appropriate actions to compensate for the interference effects.

3. For every sample analyzed, verification is necessary to determine that method of standard addition is not required (see Exhibit E).
4. If method of standard addition is required, follow the procedure given in Exhibit E).
5. The use of the Electrodeless Discharge Lamps (EDL) for the light source is recommended.

BERYLLIUM

Method 210.2 CLP-M (Atomic Absorption, furnace technique)

Optimum Concentration Range: 1-30 µg/l
Approximate Detection Limit: 0.2 µg/l

Preparation of Standard Solution

1. Stock solution: Dissolve 11.6586g of beryllium sulfate, BeSO_4 , in deionized distilled water containing 2 ml concentrated nitric acid and dilute to 1 liter. 1 ml = 1 µg Be (1000µg/L).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".
3. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec-125°C.
2. Ashing Time and Temp: 30 sec-1000°C.
3. Atomizing Time and Temp: 10 sec-2800°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 234.9 nm
6. The operating parameters should be set as specified by the particular instrument manufacturer.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer MGA-2100, based on the use of a 20 µl injection, continuous flow purge gas and non-pyrolytic graphite and are to be used as guidelines only. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is required.
3. Because of possible chemical interaction, nitrogen should not be used as a purge gas.
4. For every sample analyzed, verification is necessary to determine that method of standard addition is not required (see Exhibit E)
5. If method of standard addition is required, follow the procedure given in Exhibit E.

CADMIUM

Method 213.2 CLP-M (Atomic Absorption, furnace technique)

Optimum Concentration Range: 0.5-10 ug/l

Approximate Detection Limit: 0.1 ug/l

Preparation of Standard Solution

1. Stock solution: Carefully weigh 2.282g of cadmium sulfate, $3 \text{ Cd SO}_4 \cdot 8 \text{ H}_2\text{O}$ (analytical reagent grade) and dissolve in deionized distilled water. Make up to 1 liter with deionized distilled water. 1 mL = 1 mg Cd (1000 mg/L).
2. Ammonium Phosphate solution (40%): Dissolve 40 grams of ammonium phosphate, $(\text{NH}_4)_2\text{HPO}_4$ (analytical reagent grade) in deionized distilled water and dilute to 100 ml.
3. Prepare dilutions of stock cadmium solution to be used as calibration standards at the time of analysis. To each 100 ml of standard and sample alike add 2.0 ml of the ammonium phosphate solution. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec-125°C.
2. Ashing Time and Temp: 30 sec-500°C.
3. Atomizing Time and Temp: 10 sec-1900°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 228.8 nm
6. The operating parameters should be set as specified by the particular instrument manufacturer.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 ul injection, continuous flow purge gas and non-pyrolytic graphite and are to be used as guidelines only. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is required.
3. Contamination from the work area is critical in cadmium analysis. Use pipet tips which are free of cadmium.
4. For every sample analyzed, verification is necessary to determine that method of standard addition is not required (see Exhibit E).
5. If method of standard addition is required, follow the procedure given in Exhibit E.

CHROMIUM

Method 218.2 CLP-M (Atomic Absorption, furnace technique)

Optimum Concentration Range: 5-100 ug/l

Approximate Detection Limit: 1 ug/l

Preparation of Standard Solution

1. **Stock solution:** Prepare as described under "direct aspiration method" (Exhibit D, Attachment 4).
2. **Calcium Nitrate solution:** Dissolve 11.8 grams of calcium nitrate, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (analytical reagent grade) in deionized distilled water and dilute to 100 ml. 1 ml = 20 mg Ca.
3. Prepare dilutions of the stock chromium solution to be used as calibration standards at the time of analysis. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation. To each 100 ml of standard and sample alike, add 1 ml of 30% H_2O_2 and 1 ml of the calcium nitrate solution.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec-125°C.
2. Ashing Time and Temp: 30 sec-1000°C.
3. Atomizing Time and Temp: 10 sec-2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 357.9 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Notes

1. The above concentration values and instrument conditions are for a Perkin Elmer MGA-2100, based on the use of a 20 ul injection, continuous flow purge gas and non-pyrolytic graphite and are to be used as guidelines only.
2. Hydrogen peroxide is added to the acidified solution to convert all chromium to the trivalent state. Calcium is added to a level above 200 mg/l where its suppressive effect becomes constant up to 1000 mg/l.
3. Background correction is required.
4. Nitrogen should not be used as a purge gas because of possible CN band interference.
5. Pipet tips have been reported to be a possible source of contamination.
6. For every sample analyzed, verification is necessary to determine that method of standard addition is not required (see Exhibit E).
7. If method of standard addition is required, follow the procedure given in Exhibit E.

LEAD

Method 239.2 CLP-M (Atomic Absorption, furnace technique)

Optimum Concentration Range: 5-100 ug/l

Approximate Detection Limit: 1 ug/l

Preparation of Standard Solution

1. Stock solution: Carefully weigh 1.599 g of lead nitrate, $\text{Pb}(\text{NO}_3)_2$ (analytical reagent grade), and dissolve in deionized distilled water. When solution is complete, acidify with 10 mL redistilled HNO_3 and dilute to 1 liter with deionized distilled water. 1 mL = 1 mg Pb (1000mg/L).
2. Lanthanum Nitrate solution: Dissolve 58.64 g of ACS reagent grade La_2O_3 in 100 mL conc. HNO_3 and dilute to 1000 mL with deionized distilled water. 1 mL = 50 mg La.
3. Working Lead solution: Prepare dilutions of stock lead solution to be used as calibration standards at the time of analysis. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation. To each 100 mL of diluted standard add 10 mL of the lanthanum nitrate solution.

Sample Preparation

1. To each 100 mL of prepared sample solution add 10 mL of the lanthanum nitrate solution.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec-125°C.
2. Ashing Time and Temp: 30 sec-500°C.
3. Atomizing Time and Temp: 10 sec-2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 283.3 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 ul injection, continuous flow purge gas and non-pyrolytic graphite and are to be used as guidelines only. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.

Method 239.2 CLP-M (cont.)

2. The use of background correction is required.
3. Greater sensitivity can be achieved using the 217.0 nm line, but the optimum concentration range is reduced. The use of a lead electrodeless discharge lamp at this lower wavelength has been found to be advantageous. Also a lower atomization temperature (2400°C) may be preferred.
4. To suppress sulfate interference (up to 1500 ppm) lanthanum is added as the nitrate to both samples and calibration standards. (Atomic Absorption Newsletter Vol. 15, No. 3, p. 71, May-June 1976).
5. Since glassware contamination is a severe problem in lead analysis, all glassware should be cleaned immediately prior to use, and once cleaned, should not be open to the atmosphere except when necessary.
6. For every sample analyzed, verification is necessary to determine that method of standard addition is not required (see Exhibit E).
7. If method of standard addition is required, follow the procedure given in Exhibit E.

SELENIUM

Method 270.2 CLP-M (Atomic Absorption, furnace technique)

Optimum Concentration Range: 5-100 ug/l

Approximate Detection Limit: 2 ug/l

Preparation of Standard Solution

1. Stock Selenium solution: Dissolve 0.3453 g of selenous acid (actual assay 94.6% H_2SeO_3) in deionized distilled water and make up to 200 ml. 1 ml = 1 mg Se (1000 mg/l).
2. Nickel Nitrate solution, 5%: Dissolve 24.780 g of ACS reagent grade $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in deionized distilled water and make up to 100 ml.
3. Nickel Nitrate solution, 1%: Dilute 20 ml of the 5% nickel nitrate to 100 ml with deionized distilled water.
4. Working Selenium solution: Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation. Withdraw appropriate aliquots of the stock solution, add 1 ml of conc. HNO_3 , 2 ml of 30% H_2O_2 and 2 ml of the 5% nickel nitrate solution. Dilute to 100 ml with deionized distilled water.

Sample Preparation

1. Add 100 ul of the 5% nickel nitrate solution to 5 ml of the digested sample. The sample is now ready for injection into the furnace.

Instrument Parameters

1. Drying Time and Temp: 30 sec @ 125°C.
2. Charring Time and Temp: 30 sec @ 1200°C.
3. Atomizing Time and Temp: 10 sec @ 2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 196.0 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Method 270.2 GLP (cont.)

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer MCA-2100, based on the use of a 20 μ l injection, purge gas interrupt and non-pyrolytic graphite and are to be used as guide-lines only. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is required. Background correction made by the deuterium arc method does not adequately compensate for high levels of certain interferences (i.e., Al, Fe). If conditions occur where significant interference is suspected, the lab must switch to an alternate wavelength or take other appropriate actions to compensate for the interference effects.
3. Selenium analysis suffers interference from chlorides (>800 mg/l) and sulfate (>200 mg/l). For the analysis of industrial effluents and samples with concentrations of sulfate from 200 to 2000 mg/l, both samples and standards should be prepared to contain 1% nickel.
4. For every sample analyzed, verification is necessary to determine that method of standard addition is not required (see Exhibit E).
5. If method of standard addition is required, follow the procedure given in Exhibit E.
6. The use of the Electrodeless Discharge Lamp (EDL) for the light source is recommended.

SILVER

Method 272.2 CLP-M (Atomic Absorption, furnace technique)

Optimum Concentration Range: 1-25 ug/l
Approximate Detection Limit: 0.2 ug/l

Preparation of Standard Solution

1. Stock solution: Dissolve 1.575 g of AgNO_3 (analytical reagent grade) in deionized distilled water. Add 10 mL of concentrated HNO_3 and make up to 1 liter. 1 mL = 1 mg Ag (1000 mg/L).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".
3. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec-125°C.
2. Ashing Time and Temp: 30 sec-400°C.
3. Atomizing Time and Temp: 10 sec-2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 328.1 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 ul injection, continuous flow purge gas and non-pyrolytic graphite and are to be used as guidelines only. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is required.
3. The use of halide acids should be avoided.
4. If absorption to container walls or formation of AgCl is suspected, see NOTE 3 under the Direct Aspiration Method (Exhibit D, Attachment 4).
5. For every sample analyzed, verification is necessary to determine that method of standard addition is not required (see Exhibit E).
6. If method of standard addition is required, follow the procedure given in Exhibit E.

THALLIUM

Method 279.2 CLP-M (Atomic Absorption, furnace technique)

Optimum Concentration Range: 5-100 ng/l

Approximate Detection Limit: 1 ng/l

Preparation of Standard Solution

1. Stock solution: Dissolve 1.303g of thallium nitrate, $TlNO_3$ (analytical reagent grade) in deionized distilled water. Add 10 mL of concentrated nitric acid and dilute to 1 liter with deionized distilled water. 1 mL = 1 ng Tl (1000 ng/L).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".
3. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec @ 125°C.
2. Ashing Time and Temp: 30 sec @ 400°C.
3. Atomizing Time and Temp: 10 sec @ 2400°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 276.8 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 ul injection, continuous flow purge gas and non-pyrolytic graphite and are to be used as guidelines only. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is required.
3. Nitrogen may also be used as the purge gas.
4. For every sample analyzed, verification is necessary to determine that method of standard addition is not required (see Exhibit E).
5. If method of standard addition is required, follow the procedure given in Exhibit E.

Bibliography

1. Methods for Chemical Analysis of Water and Wastes (EPA-600/4-79-020), Metals - 4, Methods 204.2 (Sb), 206.2 (As), 210.2 (Be), 213.2 (Cd), 218.2 (Cr), 239.2 (Pb), 270.2 (Se), 272.2 (Ag) and 279.2 (Tl).

ATTACHMENT 3

Method 200.7 CLP-M* INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROMETRIC METHOD FOR TRACE ELEMENT ANALYSIS OF WATER AND WASTES

1. Scope and Application

- 1.1 Dissolved elements are determined in filtered and acidified samples. Appropriate steps must be taken in all analyses to ensure that potential interferences are taken into account. This is especially true when dissolved solids exceed 1500 mg/L. (See 5.)
- 1.2 Total elements are determined after appropriate digestion procedures are performed. Since digestion techniques increase the dissolved solids content of the samples, appropriate steps must be taken to correct for potential interference effects. (See 5.)
- 1.3 Table 1 lists elements along with recommended wavelengths and typical estimated instrumental detection limits using conventional pneumatic nebulization. Actual working detected limits are sample dependent and as the sample matrix varies, these concentrations may also vary. In time, other elements may be added as more information becomes available and as required.
- 1.4 Because of the differences between various makes and models of satisfactory instruments, no detailed instrumental operating instructions can be provided. Instead, the analyst is referred to the instructions provided by the manufacturer of the particular instrument.

2. Summary of Method

- 2.1 The method describes a technique for the simultaneous or sequential multielement determination of trace elements in solution. The basis of the method is the measurement of atomic emission by an optical spectroscopic technique. Samples are nebulized and the aerosol that is produced is transported to the plasma torch where excitation occurs. Characteristic atomic-line emission spectra are produced by a radio-frequency inductively coupled plasma (ICP). The spectra are dispersed by a grating spectrometer and the intensities of the line are monitored by photomultiplier tubes. The photocurrents from the photomultiplier tubes are processed and controlled by a computer system. A background correction technique is required to compensate for variable background contribution to the determination of trace elements. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent

to the analyte line. The position used must be free of spectral interference and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences named in 3.1 (and tests for their presence as described in 3.2) should also be recognized and appropriate corrections made.

3. Definitions

- 3.1 Dissolved** — Those elements which will pass through a 0.45 μ m membrane filter.
- 3.2 Suspended** — Those elements which are retained by a 0.45 μ m membrane filter.
- 3.3 Total** — The concentration determined on an unfiltered sample following vigorous digestion.
- 3.4 Instrumental detection limits** — See Exhibit E, pages 2 - 4.
- 3.5 Sensitivity** — The slope of the analytical curve, i.e. functional relationship between emission intensity and concentration.
- 3.6 Instrument check standard** — A multielement standard of known concentrations prepared by the analyst to monitor and verify instrument performance on a daily basis. (See 7.6.1.)
- 3.7 Interference check sample** — A solution containing both interfering and analyte elements of known concentration that can be used to verify background and interelement correction factors. (See 7.6.2.)
- 3.8 Quality control sample** — A solution obtained from an outside source having known concentration values to be used to verify the calibration standards. (See 7.6.3.)
- 3.9 Calibration standards** — A series of known standard solutions used by the analyst for calibration of the instrument (i.e., preparation of the analytical curve). (See 7.4.)
- 3.10 Linear dynamic range** — The concentration range over which the analytical curve remains linear as determined in Exhibit E.
- 3.11 Reagent blank** — A volume of deionized, distilled water containing the same acid matrix as the calibration standards carried through the entire analytical scheme. (See 7.5.2.)
- 3.12 Calibration blank** — A volume of deionized, distilled water acidified with HNO_3 and HCl . (See 7.5.1.)

3.13 Method of standard addition — The standard addition technique involves the use of the unknown and the unknown-plus-a-known amount of standard by adding known amounts of standard to one or more aliquots of the processed sample solution.

4. Safety

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material handling data sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified (11.7, 11.8 and 11.9) for the information of the analyst.

5. Interferences

5.1 Several types of interference effects may contribute to inaccuracies in the determination of trace elements. They can be summarized as follows:

5.1.1 Spectral interferences can be categorized as 1) overlap of a spectral line from another element; 2) unresolved overlap of molecular band spectra; 3) background contribution from continuous or recombination phenomena; and 4) background contribution from stray light from the line emission of high concentration elements. The first of these effects can be compensated by utilizing a computer correction of the raw data, requiring the monitoring and measurement of the interfering element. The second effect may require selection of an alternate wavelength. The third and fourth effects can usually be compensated by a background correction adjacent to the analyte line. In addition, users of simultaneous multi-element instrumentation must assume the responsibility of verifying the absence of spectral interference from an element that could occur in a sample but for which there is no channel in the instrument array. Listed in Table 2 are some interference effects for the recommended wavelengths given in Table 1. The data in Table 2 are intended for use only as a rudimentary guide for the indication of potential spectral interferences. For this purpose, linear relations between concentration and intensity for the analytes and the interferents can be assumed. The interference information, which was collected at the Ames Laboratory¹, is expressed as

¹Ames Laboratory, USDOE, Iowa State University, Ames Iowa 50011
analyte concentration equivalents (i.e., false analyte concentrations) arising from 100 mg/L of the interferent element. The suggested use of this information is as follows: Assume that arsenic (at 193.696 nm) is to be determined in a sample

containing approximately 10 mg/L of aluminum. According to Table 2, 100 mg/L of aluminum would yield a false signal for arsenic equivalent to approximately 1.3 mg/L. Therefore, 10 mg/L of aluminum would result in a false signal for arsenic equivalent to approximately 0.13 mg/L. The reader is cautioned that other analytical systems may exhibit somewhat different levels of interference than those shown in Table 2, and that the interference effects must be evaluated for each individual system. Only those interferents listed were investigated and the blank spaces in Table 2 indicate that measurable interferences were not observed from the interferent concentrations listed in Table 3. Generally, interferences were discernible if they produced peaks or background shifts corresponding to 2-5% of the peaks generated by the analyte concentrations also listed in Table 3.

At present, information on the listed silver and potassium wavelengths are not available but it has been reported that second order energy from the magnesium 383.231 nm wavelength interferes with the listed potassium line at 766.491 nm.

5.1.2 Physical interferences are generally considered to be effects associated with the sample nebulization and transport processes. Such properties as change in viscosity and surface tension can cause significant inaccuracies especially in samples which may contain high dissolved solids and/or acid concentrations. The use of a peristaltic pump may lessen these interferences. If these types of interferences are operative, they must be reduced by dilution of the sample and/or utilization of standard addition techniques. Another problem which can occur from high dissolved solids is salt buildup at the tip of the nebulizer. This affects aerosol flow rate causing instrumental drift. Wetting the argon prior to nebulization, the use of a tip washer, or sample dilution have been used to control this problem. Also, it has been reported that better control of the argon flow rate improves instrument performance. This is accomplished with the use of mass flow controllers.

5.1.3 Chemical interferences are characterized by molecular compound formation, ionization effects and solute vaporization effects. Normally these effects are not pronounced with the ICP technique, however, if observed they can be minimized by careful selection of operating conditions (that is, incident power, observation position, and so forth), by buffering of the sample, by matrix matching, and by standard addition procedures. These types of interferences can be highly dependent on matrix type and the specific analyte element.

5.2 For each group of samples of a similar matrix type and concentration (i.e., low, medium) for each case of samples, or for each 20 samples received, whichever is more frequent, the following tests must be performed prior to reporting concentration data for analyte elements.

- 5.2.1 Serial dilution -- If the analyte concentration is sufficiently high (minimally a factor of 10 above the instrument detection limit after dilution), an analysis of a 5 fold dilution must agree within 10 percent of the original determination. Samples identified as Field Blanks cannot be used for serial dilution analysis.

If the dilution analysis is not within 10%, a chemical or physical interference effect should be suspected, and the data of all samples received associated with that serial dilution must be flagged with an "E". Serial dilution results must be reported on QC Report Form IX.

6. Apparatus

6.1 Inductively Coupled Plasma-Atomic Emission Spectrometer.

- 6.1.1 Computer controlled atomic emission spectrometer with background correction.
- 6.1.2 Radiofrequency generator.
- 6.1.3 Argon gas supply, welding grade or better.

- 6.2 Operating conditions -- Because of the differences between various makes and models of satisfactory instruments, no detailed operating instructions can be provided. Instead, the analyst should follow the instructions provided by the manufacturer of the particular instrument. Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects must be investigated and established for each individual analyte line on that particular instrument. All measurements must be within the instrument linear range where correction factors are valid. It is the responsibility of the analyst to verify that the instrument configuration and operating conditions used satisfy the analytical requirements and to maintain quality control data confirming instrument performance and analytical results.

7. Reagents and standards

- 7.1 Acids used in the preparation of standards and for sample processing must be ultra-high purity grade or equivalent. Redistilled acids are acceptable.
- 7.1.1 Acetic acid, conc. (sp gr 1.06).
- 7.1.2 Hydrochloric acid, conc. (sp gr 1.19).
- 7.1.3 Hydrochloric acid, (1+1): Add 500 mL conc. HCl (sp gr 1.19) to 400 mL deionized, distilled water and dilute to 1 liter.
- 7.1.4 Nitric acid, conc. (sp gr 1.41).
- 7.1.5 Nitric acid, (1+1): Add 500 mL conc. HNO₃ (sp gr 1.41) to 400 mL deionized, distilled water and dilute to 1 liter.

7.2 Deionized, distilled water: Prepare by passing distilled water through a mixed bed of cation and anion exchange resins. Use deionized, distilled water for the preparation of all reagents, calibration standards and as dilution water. The purity of this water must be equivalent to ASTM Type II reagent water of Specification D 1193 (14.6).

7.3 Standard stock solutions may be purchased or prepared from ultra high purity grade chemicals or metals. All salts must be dried for 1 h at 105° unless otherwise specified.

(CAUTION: Many metal salts are extremely toxic and may be fatal if swallowed. Wash hands thoroughly after handling.) Typical stock solution preparation procedures follow:

7.3.1 Aluminum solution, stock, 1 mL = 100 ug Al: Dissolve 0.100 g of aluminum metal in an acid mixture of 4 mL of (1+1) HCl and 1 mL of conc. HNO₃ in a beaker. Warm gently to effect solution. When solution is complete, transfer quantitatively to a liter flask, add an additional 10 mL of (1+1) HCl and dilute to 1000 mL with deionized, distilled water.

7.3.2 Antimony solution stock, 1 mL = 100 ug Sb: Dissolve 0.2669 g K(SbO)C₄H₄O₆ in deionized distilled water, add 10 mL (1+1) HCl and dilute to 1000 mL with deionized, distilled water.

7.3.3 Arsenic solution, stock, 1 mL = 100 ug As: Dissolve 0.1320 g of As₂O₃ in 100 mL of deionized, distilled water containing 0.4 g NaOH. Acidify the solution with 2 mL conc. HNO₃ and dilute to 1,000 mL with deionized, distilled water.

7.3.4 Barium solution, stock, 1 mL = 100 ug Ba: Dissolve 0.1516 g BaCl₂ (dried at 250°C for 2 hrs) in 10 mL deionized, distilled water with 1 mL (1+1) HCl. Add 10.0 mL (1+1) HCl and dilute to 1,000 mL with deionized, distilled water.

7.3.5 Beryllium solution, stock, 1 mL = 100 ug Be: Do not dry. Dissolve 1.966 g BeSO₄·4H₂O, in deionized, distilled water, add 10.0 mL conc. HNO₃ and dilute to 1,000 mL with deionized, distilled water.

7.3.6 Boron solution, stock, 1 mL = 100 ug B: Do not dry. Dissolve 0.5716 g anhydrous H₃BO₃ in deionized, distilled water and dilute to 1,000 mL. Use a reagent meeting ACS specifications, keep the bottle tightly stoppered and store in a desiccator to prevent the entrance of atmospheric moisture.

7.3.7 Cadmium solution, stock, 1 mL = 100 ug Cd: Dissolve 0.1142 g CdO in a minimum amount of (1+1) HNO₃. Heat to increase rate of dissolution. Add 10.0 mL conc. HNO₃ and dilute to 1,000 mL with deionized, distilled water.

- 7.3.8 Calcium solution, stock, 1 mL = 100 ug Ca: Suspend 0.2498 g CaCO_3 dried at 180°C for 1 h before weighing in deionized, distilled water and dissolve cautiously with a minimum amount of (1+1) HNO_3 . Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.
- 7.3.9 Chromium solution, stock, 1 mL = 100 ug Cr: Dissolve 0.1923 g of CrO_3 in deionized, distilled water. When solution is complete acidify with 10 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.
- 7.3.10 Cobalt solution stock, 1 mL = 100 ug Co: Dissolve 0.1000 g of cobalt metal in a minimum amount of (1+1) HNO_3 . Add 10.0 mL (1+1) HCl and dilute to 1,000 mL with deionized, distilled water.
- 7.3.11 Copper solution, stock, 1 mL = 100 ug Cu: Dissolve 0.1252 g CuO in a minimum amount of (1+1) HNO_3 . Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.
- 7.3.12 Iron solution, stock, 1 mL = 100 ug Fe: Dissolve 0.1430 g Fe_2O_3 in a warm mixture of 20 mL (1+1) HCl and 2 mL of conc. HNO_3 . Cool, add an additional 5 mL of conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.
- 7.3.13 Lead solution, stock, 1 mL = 100 ug Pb: Dissolve 0.1599 g $\text{Pb}(\text{NO}_3)_2$ in a minimum amount of (1+1) HNO_3 . Add 10.0 mL of conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.
- 7.3.14 Magnesium solution, stock, 1 mL = 100 ug Mg: Dissolve 0.1658 g MgO in a minimum amount of (1+1) HNO_3 . Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.
- 7.3.15 Manganese solution, stock, 1 mL = 100 ug Mn: Dissolve 0.1000 g of manganese metal in the acid mixture, 10 mL conc. HCl and 1 mL conc. HNO_3 , and dilute to 1,000 mL with deionized, distilled water.
- 7.3.16 Molybdenum solution, stock, 1 mL = 100 ug Mo: Dissolve 0.2043 g $(\text{NH}_4)_2\text{MoO}_4$ in deionized, distilled water and dilute to 1,000 mL.
- 7.3.17 Nickel solution, stock, 1 mL = 100 ug Ni: Dissolve 0.1000 g of nickel metal in 10 mL hot conc. HNO_3 , cool and dilute to 1,000 mL with deionized, distilled water.
- 7.3.18 Potassium solution, stock, 1 mL = 100 ug K: Dissolve 0.1907 g KCl , dried at 110°C, in deionized, distilled water. Dilute to 1,000 mL.

- 7.3.19 Selenium solution, stock, 1 mL = 100 ug Se: Do not dry. Dissolve 0.1727 g H_2SeO_3 (actual assay 94.6%) in deionized, distilled water and dilute to 1,000 mL.
- 7.3.20 Silica solution, stock, 1 mL = 100 ug SiO_2 : Do not dry. Dissolve 0.4730 g $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ in deionized, distilled water. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.
- 7.3.21 Silver solution, stock, 1 mL = 100 ug Ag : Dissolve 0.1575 g AgNO_3 in 100 mL of deionized, distilled water and 10 mL conc. HNO_3 . Dilute to 1,000 mL with deionized, distilled water.
- 7.3.22 Sodium solution, stock, 1 mL = 100 ug Na: Dissolve 0.2542 g NaCl in deionized, distilled water. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.
- 7.3.23 Thallium solution, stock, 1 mL = 100 ug Tl: Dissolve 0.1303 g TlNO_3 in deionized, distilled water. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.
- 7.3.24 Vanadium solution, stock, 1 mL = 100 ug V: Dissolve 0.2297 NH_4VO_3 in a minimum amount of conc. HNO_3 . Heat to increase rate of dissolution. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.
- 7.3.25 Zinc solution, stock, 1 mL = 100 ug Zn: Dissolve 0.1245 g ZnO in a minimum amount of dilute HNO_3 . Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.
- 7.4 Mixed calibration standard solutions — Prepare mixed calibration standard solutions by combining appropriate volumes of the stock solutions in volumetric flasks. (See 7.4.1 thru 7.4.5.) Add 2 mL of (1+1) HNO_3 and 10 mL of (1+1) HCl and dilute to 100 mL with deionized, distilled water. (See Notes 1 and 6.) Prior to preparing the mixed standards, each stock solution should be analyzed separately to determine possible spectral interference or the presence of impurities. Care should be taken when preparing the mixed standards that the elements are compatible and stable. Transfer the mixed standard solutions to a FEP fluorocarbon or unused polyethylene bottle for storage. Fresh mixed standards should be prepared as needed with the realization that concentration can change on aging. Calibration standards must be initially verified using a quality control sample and monitored weekly for stability (see 7.6.3). Although not specifically required, some typical calibration standard combinations follow when using those specific wavelengths listed in Table 1.
- 7.4.1 Mixed standard solution I — Manganese, beryllium, cadmium, lead, and zinc.
- 7.4.2 Mixed standard solution II — Barium, copper, iron, vanadium, and cobalt.

- 7.4.3 Mixed standard solution III — Molybdenum, silica, arsenic, and selenium.
- 7.4.4 Mixed standard solution IV — Calcium, sodium, potassium, aluminum, chromium and nickel.
- 7.4.5 Mixed standard solution V — Antimony, boron, magnesium, silver, and thallium.

NOTE 1: If the addition of silver to the recommended acid combination results in an initial precipitation add 15 mL of deionized distilled water and warm the flask until the solution clears. Cool and dilute to 100 mL with deionized, distilled water. For this acid combination the silver concentration should be limited to 2 mg/L. Silver under these conditions is stable in a tap water matrix for 30 days. Higher concentrations of silver require additional HCl.

- 7.5 Two types of blanks are required for the analysis. The calibration blank (3.13) is used in establishing the analytical curve while the reagent blank (preparation blank, 3.12) is used to correct for possible contamination resulting from varying amounts of the acids used in the sample processing.
 - 7.5.1 The calibration blank is prepared by diluting 2 mL of (1+1) HNO_3 and 10 mL of (1+1) HCl to 100 mL with deionized, distilled water. (See Note 6.) Prepare a sufficient quantity to be used to flush the system between standards and samples.
 - 7.5.2 The reagent blank (or preparation blank - See Exhibit E) must contain all the reagents and in the same volumes as used in the processing of the samples. The reagent blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis.
- 7.6 In addition the calibration standards, an instrument check standard (3.6), an interference check sample (3.7) and a quality control sample (3.8) are also required for the analyses.
 - 7.6.1 The instrument check standard for continuing calibration verification is prepared by the analyst by combining compatible elements at a concentration equivalent to the mid-point of their respective calibration curves. (See 10.1.3.)
 - 7.6.2 The interference check sample is prepared by the analyst, or obtained from EPA if available (Exhibit E).
 - 7.6.3 The quality control sample for the initial calibration verification should be prepared in the same acid matrix as the calibration standards and in accordance with the

instructions provided by the supplier. EPA will either supply a quality control sample or information where one of equal quality can be procured. (See 10.1.1.)

8. Procedure

- 8.1 Set up instrument with proper operating parameters established in Section 6.2. The instrument must be allowed to become thermally stable before beginning. This usually requires at least 30 min. of operation prior to calibration.
- 8.2 Initiate appropriate operating configuration of computer.
- 8.3 Profile and calibrate instrument according to instrument manufacturer's recommended procedures, using mixed calibration standard solutions such as those described in Section 7.4. Flush the system with the calibration blank (7.5.1) between each standard. (See NOTE 7.) Use the average intensity of multiple exposures for both standardization and sample analysis to reduce random error, a minimum of two replicate exposures are required.

NOTE 7: For boron concentrations greater than 500 ug/L extended flush times of 1 to 2 minutes may be required.

- 8.4 Begin the sample run flushing the system with the calibration blank solution (7.5.1) between each sample. (See NOTE 7.) Analyze the instrument check standard (7.6.1) and the calibration blank (7.5.1) each 10 samples.

9. Calculation

- 9.1 Reagent blanks (preparation blanks) should be treated as specified in Exhibit E.
- 9.2 If dilutions were performed, the appropriate factor must be applied to sample values.
- 9.3 Units must be clearly specified.

10. Quality Control (Instrumental)

- 10.1 Check the instrument standardization by analyzing appropriate quality control check standards as follows:
 - 10.1.1 A quality control sample (7.6.3) must be used daily for the initial calibration verification (See Exhibit E). A fresh dilution of this sample shall be analyzed every week thereafter to monitor their stability. If the results are not within +10% of the true value listed for the control sample, prepare a new calibration standard and recalibrate the instrument. If this does not correct the problem, prepare a new stock standard and a new calibration standard and repeat the calibration.

10.1.2 Analyze the calibration blank (7.5.1) at a frequency of 10%. The result should be within \pm contract required detection levels (Exhibit C). If the result is not within the control level, terminate the analysis, correct the problem and recalibrate the instrument (See Exhibit E).

10.1.3 For continuing calibration verification, analyze an appropriate instrument check standard (7.6.1) containing the elements of interest at a frequency of 10%. This check standard is used to determine instrument drift. If agreement is not within 10% of the expected values, the analysis is out of control. The analysis must be terminated, the problem corrected, the instrument recalibrated, and the preceding 10 samples reanalyzed (See Exhibit E).

10.1.4 To verify interelement and background correction factors analyze the ICP interference check sample (7.6.2) at the beginning, and end of the sample run or a minimum of twice per 8 hour work shift whichever is more frequent. The check sample must be analyzed initially at least 5 times repetitively to establish a mean value and standard deviation. Results must fall within the established control limits. If not, terminate the analysis, correct the problem, recalibrate the instrument, and reanalyze the samples (See Exhibit E).

11. Bibliography

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8. "OSHA Safety and Health Standards, General Industry," (29 CFR 1910), Occupational Safety and Health Administration, OSHA 2206, (Revised, January 1976).
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TABLE 1 - RECOMMENDED WAVELENGTHS⁽²⁾ AND ESTIMATED INSTRUMENTAL DETECTION LIMITS

Element	Wavelength, nm ⁽¹⁾	Estimated Detection Limit, ug/L ⁽²⁾
Aluminum	308.215	45
Antimony	206.833	32 ^f
Arsenic	193.696	53
Barium	455.403	2
Beryllium	313.042	0.3
Boron	249.773	5
Cadmium	226.502	4
Calcium	317.933	10
Chromium	267.716	7
Cobalt	228.616	7
Copper	324.754	6
Iron	259.940	7
Lead	220.353	42
Magnesium	279.079	30
Manganese	257.610	2
Molybdenum	202.030	8
Nickel	231.604	15
Potassium	766.491	see ⁽³⁾
Selenium	196.026	75
Silica (SiO ₂)	288.158	58
Silver	328.068	7
Sodium	588.995	29
Thallium	190.864	40
Vanadium	292.402	8
Zinc	213.856	2

- (1) The wavelengths listed are recommended because of their sensitivity and overall acceptance. Other wavelength may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference. (See 5.1.1). The use of alternate wavelengths must be reported (in nm) with the sample data.
- (2) The estimated instrumental detection limits as shown are taken from "Inductively Coupled Plasma-Atomic Emission Spectroscopy-Prominent Lines," EPA-600/4-79-017. They are given as a guide for an instrumental limit. The actual method detection limits are sample dependent and may vary as the sample matrix varies.
- (3) highly dependent on operating conditions and plasma position.

TABLE 2. EXAMPLE OF ANALYTE CONCENTRATION EQUIVALENTS (mg/L) ARISING FROM INTERFERENTS AT THE 100 mg/L LEVEL.

Analyte	Wavelength, nm	Interferent									
		Al	Ca	Cr	Cu	Fe	Hg	Mn	Ni	Tl	V
Aluminum	308.215	--	--	--	--	--	--	0.21	--	--	1.4
Antimony	206.833	0.47	--	2.9	--	0.08	--	--	--	.25	0.45
Arsenic	193.696	1.3	--	0.44	--	--	--	--	--	--	1.1
Barium	455.403	--	--	--	--	--	--	--	--	--	--
Beryllium	313.042	--	--	--	--	--	--	--	--	0.04	0.05
Boron	249.773	0.04	--	--	--	0.32	--	--	--	--	--
Cadmium	226.502	--	--	--	--	0.03	--	--	0.02	--	--
Calcium	317.933	--	--	0.08	--	0.01	0.01	0.04	--	0.03	0.03
Chromium	267.716	--	--	--	--	0.003	--	0.04	--	--	0.04
Cobalt	228.616	--	--	0.03	--	0.005	--	--	0.03	0.15	--
Copper	324.754	--	--	--	--	0.003	--	--	--	0.05	0.02
Iron	259.940	--	--	--	--	--	--	0.12	--	--	--
Lead	220.353	0.17	--	--	--	--	--	--	--	--	--
Magnesium	279.079	--	0.02	0.11	--	0.13	--	0.25	--	0.07	0.12
Manganese	257.610	0.005	--	0.01	--	0.002	0.002	--	--	--	--
Molybdenum	202.030	0.05	--	--	--	0.03	--	--	--	--	--
Nickel	231.604	--	--	--	--	--	--	--	--	--	--
Selenium	196.026	0.23	--	--	--	0.09	--	--	--	--	--
Silicon	288.158	--	--	0.07	--	--	--	--	--	--	0.01
Sodium	588.995	--	--	--	--	--	--	--	--	0.08	--
Thallium	190.864	0.10	--	--	--	--	--	--	--	--	--
Vanadium	292.402	--	--	0.05	--	0.005	--	--	--	0.02	--
Zinc	213.856	--	--	--	0.14	--	--	--	0.29	--	--

TABLE 3. INTERFERENT AND ANALYTE ELEMENTAL CONCENTRATIONS USED
FOR INTERFERENCE MEASUREMENTS IN TABLE 2 (EXHIBIT D)

Analytes	(mg/L)	Interferents	(mg/L)
Al	10	Al	1000
As	10	Ca	1000
B	10	Cr	200
Ba	1	Cu	200
Be	1	Fe	1000
Ca	1	Mg	1000
Cd	10	Mn	200
Co	1	Ni	200
Cr	1	Ti	200
Cu	1	V	200
Fe	1		
Mg	1		
Mn	1		
Mo	10		
Na	10		
Ni	10		
Pb	10		
Sb	10		
Se	10		
Si	1		
Tl	10		
V	1		
Zn	10		

ATTACHMENT 4
CALCIUM

Method 215.1 CLP-M* (Atomic Absorption, direct aspiration)

Optimum Concentration Range: 0.2-7 mg/l using a wavelength of 422.7 nm
Sensitivity: 0.08 mg/l
Detection Limit: 0.01 mg/l

Preparation of Standard Solution

1. Stock Solution: Suspend 1.250 g of CaCO_3 (analytical reagent grade), dried at 180°C for 1 hour before weighing, in deionized distilled water and dissolve cautiously with a minimum of dilute HCl. Dilute to 1000 ml with deionized distilled water. 1 ml = 0.5 mg Ca (500 mg/l).
2. Lanthanum chloride solution: Dissolve 29 g of La_2O_3 , slowly and in small portions, in 250 ml conc. HCl (Caution: Reaction is violent) and dilute to 500 ml with deionized distilled water.
3. Prepare dilutions of the stock calcium solutions to be used as calibration standards at the time of analysis. To each 10 ml of calibration standard and sample alike add 1.0 ml of the lanthanum chloride solution, i.e., 20 ml of standard or sample + 2 ml LaCl_3 = 22 ml.

Instrumental Parameters (General)

1. Calcium hollow cathode lamp
2. Wavelength: 422.7 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Reducing

Notes

1. Phosphate, sulfate and aluminum interfere but are masked by the addition of lanthanum. Because low calcium values result if the pH of the sample is above 7, both standards and samples are prepared in dilute hydrochloric acid solution. Concentrations of magnesium greater than 1000 mg/l also cause low calcium values. Concentrations of up to 500 mg/l each of sodium, potassium and nitrate cause no interference.
2. Anionic chemical interferences can be expected if lanthanum is not used in samples and standards.
3. The nitrous oxide-acetylene flame will provide two to five times greater sensitivity and freedom from chemical interferences. Ionization interferences should be controlled by adding a large amount of alkali to the sample and standards. The analysis appears to be free from chemical suppressions in the nitrous oxide-acetylene flame. (Atomic Absorption Newsletter 14, 29 [1975]).
4. The 239.9 nm line may also be used. This line has a relative sensitivity of 120.

MAGNESIUM

Method 242.1 CLP-M* (Atomic Absorption, direct aspiration)

Optimum Concentration Range: 0.02-0.5 mg/l using a wavelength of 285.2 nm

Sensitivity: 0.007 mg/l

Detection Limit: 0.001 mg/l

Preparation of Standard Solution

1. Stock Solution: Dissolve 0.829 g of magnesium oxide, MgO (analytical reagent grade), in 10 ml of redistilled HNO₃ and dilute to 1 liter with deionized distilled water. 1 ml = 0.50 mg Mg (500 mg/l).
2. Lanthanum chloride solution: Dissolve 29 g of La₂O₃, slowly and in small portions in 250 ml concentrated HCl (Caution: Reaction is violent), and dilute to 500 ml with deionized distilled water.
3. Prepare dilutions of the stock magnesium solution to be used as calibration standards at the time of analysis. To each 10 ml volume of calibration standard and sample alike add 1.0 ml of the lanthanum chloride solution, i.e., 20 ml of standard or sample + 2 ml LaCl₃ = 22 ml.

Instrumental Parameters (General)

1. Magnesium hollow cathode lamp
2. Wavelength: 285.2 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Oxidizing

Notes

1. The interference caused by aluminum at concentrations greater than 2 mg/l is masked by addition of lanthanum. Sodium, potassium and calcium cause no interference at concentrations less than 400 mg/l.
2. The following line may also be used:
202.5 nm Relative Sensitivity 25
3. To cover the range of magnesium values normally observed in surface waters (0.1-20 mg/l), it is suggested that either the 202.5 nm line be used or the burner head be rotated. A 90° rotation of the burner head will produce approximately one-eighth the normal sensitivity.

POTASSIUM

Method 258.1 CLP-M* (Atomic Absorption, direct aspiration)

Optimum Concentration Range: 0.1-2 mg/l using a wavelength of 766.5 nm

Sensitivity: 0.04 mg/l

Detection Limit: 0.01 mg/l

Preparation of Standard Solution

1. Stock Solution: Dissolve 0.1907 g of KCl (analytical reagent grade), dried at 110°C, in deionized distilled water and make up to 1 liter. 1 ml = 0.10 mg K (100 mg/l).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed either directly or after processing.

Instrumental Parameters (General)

1. Potassium hollow cathode lamp
2. Wavelength: 766.5 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Slightly oxidizing

Notes

1. In air-acetylene or other high temperature flames (>2800°C), potassium can experience partial ionization which indirectly affects absorption sensitivity. The presence of other alkali salts in the sample can reduce this ionization and thereby enhance analytical results. The ionization suppressive effect of sodium is small if the ratio of Na to K is under 10. Any enhancement due to sodium can be stabilized by adding excess sodium (1000 ug/ml) to both sample and standard solutions. If more stringent control of ionization is required, the addition of cesium should be considered. Reagent blanks must be analyzed to correct for potassium impurities in the buffer zone.
2. The 404.4 nm line may also be used. This line has a relative sensitivity of 500.
3. To cover the range of potassium values normally observed in surface waters (0.1-20 mg/l), it is suggested that the burner head be rotated. A 90° rotation of the burner head provides approximately one-eighth the normal sensitivity.

SODIUM

Method 273.1 CLP-M* (Atomic Absorption, direct aspiration)

Optimum Concentration Range: 0.03-1 mg/l using a wavelength of 589.6 nm

Sensitivity: 0.015 mg/l

Detection Limit: 0.002 mg/l

Preparation of Standard Solutions

1. Stock Solution: Dissolve 2.542 g of NaCl (analytical reagent grade), dried at 140°C, in deionized distilled water and make up to 1 liter.
1 ml = 1 mg Na (1000 mg/l).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed either directly or after processing.

Instrumental Parameters (General)

1. Sodium hollow cathode lamp
2. Wavelength: 589.6 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Oxidizing

Notes

1. The 330.2 nm resonance line of sodium, which has a relative sensitivity of 185, provides a convenient way to avoid the need to dilute more concentrated solutions of sodium.
2. Low-temperature flames increase sensitivity by reducing the extent of ionization of this easily ionized metal. Ionization may also be controlled by adding potassium (1000 mg/l) to both standards and samples.

Bibliography

1. "Interim Methods for the Sampling and Analysis of Priority Pollutants in Sediments and Fish Tissue," USEPA Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, August 1977, Revised October 1980.
2. Op. Cit. (#1), Methods 215.1 (Ca), 242.1 (Mg), 258.1 (K), 2733.1 (Na).

ATTACHMENT 5

MERCURY

Method 245.1 CLP-M* (Manual Cold Vapor Technique)

1. Scope and Application

- 1.1 In addition to inorganic forms of mercury, organic mercurials may also be present. These organo-mercury compounds will not respond to the cold vapor atomic absorption technique unless they are first broken down and converted to mercuric ions. Potassium permanganate oxidizes many of these compounds, but recent studies have shown that a number of organic mercurials, including phenyl mercuric acetate and methyl mercuric chloride, are only partially oxidized by this reagent. Potassium persulfate has been found to give approximately 100% recovery when used as the oxidant with these compounds. Therefore, a persulfate oxidation step following the addition of the permanganate has been included to insure that organo-mercury compounds, if present, will be oxidized to the mercuric ion before measurement. A heat step is required for methyl mercuric chloride when present in or spiked to a natural system. For distilled water the heat step is not necessary.
- 1.2 The range of the method may be varied through instrument and/or recorder expansion. Using a 100 ml sample, a detection limit of 0.2 ug Hg/l can be achieved (see Appendix 11.2).

2. Summary of Method

- 2.1 The flameless AA procedure is a physical method based on the absorption of radiation at 253.7 nm by mercury vapor. Organic mercury compounds are oxidized and the mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration and recorded in the usual manner.

*CLP-M modified for the Contract Laboratory Program

3. Sample Handling and Preservation

- 3.1 Until more conclusive data are obtained, samples should be preserved by acidification with nitric acid to a pH of 2 or lower immediately at the time of collection.

4. Interference

- 4.1 Possible interference from sulfide is eliminated by the addition of potassium permanganate. Concentrations as high as 20 mg/l of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from distilled water.
- 4.2 Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/l had no effect on recovery of mercury from spiked samples.
- 4.3 Sea waters, brines and industrial effluents high in chlorides require additional permanganate (as much as 25 ml). During the oxidation step, chlorides are converted to free chlorine which will also absorb radiation of 253 nm. Care must be taken to assure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 ml). In addition, the dead air space in the BOD bottle must be purged before the addition of stannous sulfate. Both inorganic and organic mercury spikes have been quantitatively recovered from the sea water using this technique.
- 4.4 Interference from certain volatile organic materials which will absorb at this wavelength is also possible. A preliminary run without reagents should determine if this type of interference is present (see Appendix 11.1).

5. Apparatus

- 5.1 Atomic Absorption Spectrophotometer: (See Note 1) Any atomic absorption unit having an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed.
- NOTE 1: Instruments designed specifically for the measurement of mercury using the cold vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

Method 245.1 CLP-M (cont.)

- 5.2 Mercury Hollow Cathode Lamp: Westinghouse WL-22847, argon filled, or equivalent.
- 5.3 Recorder: Any multi-range variable speed recorder that is compatible with the UV detection system is suitable.
- 5.4 Absorption Cell: Standard spectrophotometer cells 10 cm long, having quartz end windows may be used. Suitable cells may be constructed from plexiglass tubing, 1" O.D. X 4-1/2". The ends are ground perpendicular to the longitudinal axis and quartz windows (1" diameter X 1/16" thickness) are cemented in place. The cell is strapped to a burner for support and aligned in the light beam by use of two 2" by 2" cards. One inch diameter holes are cut in the middle of each card; the cards are then placed over each end of the cell. The cell is then positioned and adjusted vertically and horizontally to find the maximum transmittance.
- 5.5 Air Pump: Any peristaltic pump capable of delivering 1 liter of air per minute may be used. A Masterflex pump with electronic speed control has been found to be satisfactory.
- 5.6 Flowmeter: Capable of measuring an air flow of 1 liter per minute.
- 5.7 Aeration Tubing: A straight glass fit having a coarse porosity. Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return.
- 5.8 Drying Tube: 6" X 3/4" diameter tube containing 20 g of magnesium perchlorate (see Note 2). The apparatus is assembled as shown in Figure 1.

NOTE 2: In place of the magnesium perchlorate drying tube, a small reading lamp with 60W bulb may be used to prevent condensation of moisture inside the cell. The lamp is positioned to shine on the absorption cell maintaining the air temperature in the cell about 10°C above ambient.

6. Reagents

- 6.1 Sulfuric Acid, Conc: Reagent grade.
 - 6.1.1 Sulfuric acid, 0.5 N: Dilute 14.0 ml of conc. sulfuric acid to 1.0 liter.
- 6.2 Nitric Acid, Conc: Reagent grade of low mercury content (see Note 3). NOTE 3: If a high reagent blank is obtained, it may be necessary to distill the nitric acid.

Method 245.1 CLP-M (cont.)

- 6.3 Stannous Sulfate: Add 25 g stannous sulfate to 250 ml of 0.5 N sulfuric acid. This mixture is a suspension and should be stirred continuously during use. (Stannous chloride may be used in place of stannous sulfate.)
- 6.4 Sodium Chloride-Hydroxylamine Sulfate Solution: Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in distilled water and dilute to 100 ml. (Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.)
- 6.5 Potassium Permanganate: 5% solution, w/v. Dissolve 5 g of potassium permanganate in 100 ml of distilled water.
- 6.6 Potassium Persulfate: 5% solution, w/v. Dissolve 5 g of potassium persulfate in 100 ml of distilled water.
- 6.7 Stock Mercury Solution: Dissolve 0.1354 g of mercuric chloride in 75 ml of distilled water. Add 10 ml of conc. nitric acid and adjust the volume to 100.0 ml. 1 ml = 1 mg Hg.

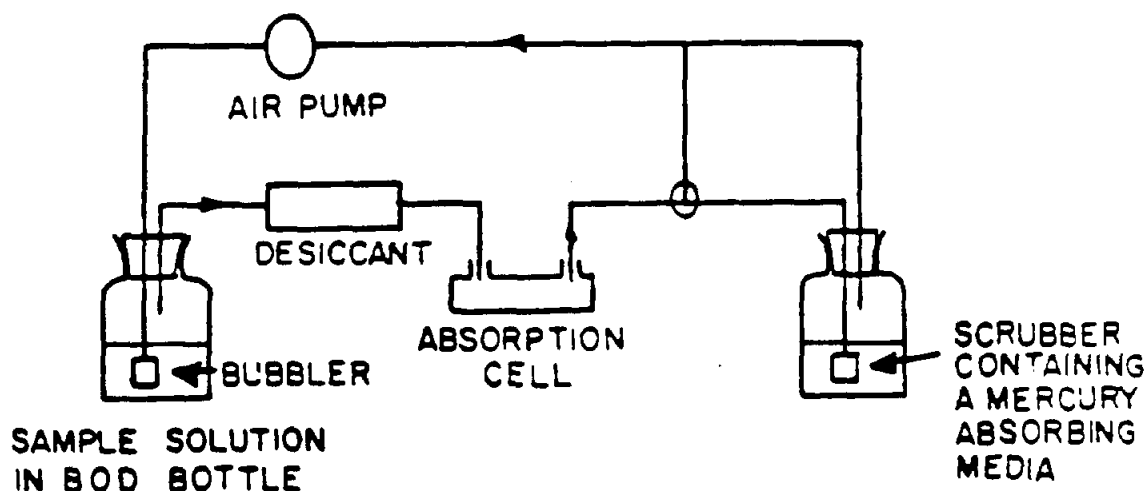


Figure 1. Apparatus for Flameless Mercury Determination.

Method 245.1 CLP-M (cont.)

- 6.8 Working Mercury Solution: Make successive dilutions of the stock mercury solution to obtain a working standard containing 0.1 ug per ml. This working standard and the dilutions of the stock mercury solution should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask as needed before the addition of the aliquot.

7. Calibration

- 7.1 Transfer 0, 0.5, 1.0, 5.0 and 10.0 ml aliquots of the working mercury solution containing 0 to 1.0 ug of mercury to a series of 300 ml BOD bottles. Add enough distilled water to each bottle to make a total volume of 100 ml. Mix thoroughly and add 5 ml of conc. sulfuric acid (6.1) and 2.5 ml of conc. nitric acid (6.2) to each bottle. Add 15 ml of KMnO_4 (6.5) solution to each bottle and allow to stand at least 15 minutes. Add 8 ml of potassium persulfate (6.6) to each bottle and heat for 2 hours in a water bath maintained at 95°C. Alternatively, cover the BOD bottles with foil and heat in an autoclave for 15 minutes at 120°C and 15 lbs. Cool and add 6 ml of sodium chloride-hydroxylamine sulfate solution (6.4) to reduce the excess permanganate. When the solution has been decolorized wait 30 seconds, add 5 ml of the stannous sulfate solution (6.3) and immediately attach the bottle to the aeration apparatus forming a closed system. At this point the sample is allowed to stand quietly without manual agitation. The circulating pump, which has previously been adjusted to a rate of 1 liter per minute, is allowed to run continuously (see Note 4). The absorbance will increase and reach maximum within 30 seconds. As soon as the recorder pen levels off, approximately 1 minute, open the bypass valve and continue the aeration until the absorbance returns to its minimum value (see Note 5). Close the bypass valve, remove the stopper and frit from the BOD bottle and continue the aeration. Proceed with the standards and construct a standard curve by plotting peak height versus micrograms of mercury.

NOTE 4: An open system where the mercury vapor is passed through the absorption cell only once may be used instead of the closed system.

NOTE 5: Because of the toxic nature of mercury vapor precaution must be taken to avoid its inhalation. Therefore, a bypass has been included in the system to either vent the mercury vapor into an exhaust hood or pass the vapor through some absorbing media, such as:

- a) equal volumes of 0.1 M KMnO_4 , and 10% H_2SO_4
- b) 0.25% iodine in a 3% KI solution

Method 245.1 CLP-M (cont.)

A specially treated charcoal that will adsorb mercury vapor is also available from Barnebey and Cheney, E. 8th Ave. and N. Cassidy St., Columbus, Ohio 43219, Cat #580-13 or #580-22.

8. Procedure

- 8.1 Transfer 100 ml, or an aliquot diluted to 100 ml, containing not more than 1.0 ug of mercury, to a 300 ml BOD bottle. Add 5 ml of sulfuric acid (6.1) and 2.5 ml of conc. nitric acid (6.2) mixing after each addition. Add 15 ml of potassium permanganate solution (6.5) to each sample bottle (see Note 6). For sewage samples additional permanganate may be required. Shake and add additional portions of potassium permanganate solution, if necessary, until the purple color persists for at least 15 minutes. Add 8 ml of potassium persulfate (6.6) to each bottle and heat for 2 hours in a water bath at 95°C.

NOTE 6: The same amount of $KMnO_4$ added to the samples should be present in standards and blanks.

Cool and add 6 ml of sodium chloride-hydroxylamine sulfate (6.4) to reduce the excess permanganate (see Note 7). After a delay of at least 30 seconds add 5 ml of stannous sulfate (6.3) and immediately attach the bottle to the aeration apparatus. Continue as described under Calibration.

NOTE 7: Add reductant in 6 mL increments until $KMnO_4$ is completely reduced.

9. Calculation

- 9.1 Determine the peak height of the unknown from the chart and read the mercury value from the standard curve.
- 9.2 Calculate the mercury concentration in the sample by the formula:

$$\text{ug Hg/l} = \frac{\text{ug Hg in aliquot}}{\text{volume of aliquot in ml}} \times \frac{1,000}{1}$$

- 9.3 Report mercury concentrations as follows: Below 0.2 ug/l, 0.2U; between 0.2 and 10 ug/l, one decimal; above 10 ug/l, whole numbers.

10. Appendix

- 10.1 While the possibility of absorption from certain organic substances actually being present in the sample does exist, EMSL has not encountered such samples. This is mentioned only to caution the analyst

Method 245.1 CLP-M (cont.)

of the possibility. A simple correction that may be used is as follows: If an interference has been found to be present (4.4), the sample should be analyzed both by using the regular procedure and again under oxidizing conditions only, that is without the reducing reagents. The true mercury value can then be obtained by subtracting the two values.

- 10.2 If additional sensitivity is required, a 200 ml sample with recorder expansion may be used provided the instrument does not produce undue noise. Using a Coleman MAS-50 with a drying tube of magnesium perchlorate and a variable recorder, 2 mv was set to read full scale. With these conditions, and distilled water solutions of mercuric chloride at concentrations of 0.15, 0.10, 0.05 and 0.025 ug/l the standard deviations were ± 0.027 , ± 0.0066 , ± 0.01 and ± 0.004 . Percent recoveries at these levels were 107, 83, 84 and 96%, respectively.
- 10.3 Directions for the disposal of mercury-containing wastes are given in ASTM Standards, Part 31, "Water", p. 349, Method D3223 (1976).

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3. Standard Methods for the Examination of Water and Wastewater 14th Edition, p. 156 (1975).

ATTACHMENT 5A

MERCURY

Method 245.2 CLP-M* (Automated Cold Vapor Technique)

1. Scope and Application

- 1.1 The working range is 0.2 to 20.0 ug Hg/l.

2. Summary of Method

- 2.1 The flameless AA procedure is a physical method based on the absorption of radiation at 253.7 nm by mercury vapor. The mercury is reduced to the elemental state and aerated from solution. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration and recorded in the usual manner.
- 2.2 In addition to inorganic forms of mercury, organic mercurials may also be present. These organo-mercury compounds will not respond to the flameless atomic absorption technique unless they are first broken down and converted to mercuric ions. Potassium permanganate oxidizes many of these compounds, but recent studies have shown that a number of organic mercurials, including phenyl mercuric acetate and methyl mercuric chloride, are only partially oxidized by this reagent. Potassium persulfate has been found to give approximately 100% recovery when used as the oxidant with these compounds. Therefore, an automated persulfate oxidation step following the automated addition of the permanganate has been included to insure that organo-mercury compounds, if present, will be oxidized to the mercuric ion before measurement.

3. Sample Handling and Preservation

- 3.1 Until more conclusive data are obtained, samples should be preserved by acidification with nitric acid to a pH of 2 or lower immediately at the time of collection(1) (see Exhibit F).

* CLP-M Modified for the contract Laboratory Program

Method 245.2 CLP-M (cont.)

4. Interference (see NOTE 1)

- 4.1 Some sea waters and waste-waters high in chlorides have shown a positive interference, probably due to the formation of free chlorine.
- 4.2 Interference from certain volatile organic materials which will absorb at this wavelength is also possible. A preliminary run under oxidizing conditions, without stannous sulfate, would determine if this type of interference is present.
- 4.3 Formation of a heavy precipitate, in some wastewaters and effluents, has been reported upon addition of concentrated sulfuric acid. If this is encountered, the problem sample cannot be analyzed by this method.
- 4.4 Samples containing solids must be blended and then mixed while being sampled if total mercury values are to be reported.

NOTE 1: All the above interferences can be overcome by use of the Manual Mercury method.

5. Apparatus

- 5.1 Technicon Auto Analyzer or equivalent instrumentation consisting of:
 - 5.1.1 Sampler II with provision for sample mixing.
 - 5.1.2 Manifold.
 - 5.1.3 Proportioning Pump II or III.
 - 5.1.4 High temperature heating bath with two distillation coils (Technicon Part #116-0163) in series.
- 5.2 Vapor-liquid separator (Figure 1).
- 5.3 Absorption cell, 100 mm long, 10 mm diameter with quartz windows.
- 5.4 Atomic Absorption Spectrophotometer (see Note 2): Any atomic absorption unit having an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed.

NOTE 2: Instruments designed specifically for the measurement of mercury using the cold vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

- 5.5 Mercury Hollow Cathode Lamp: Westinghouse WL-22847, argon filled, or equivalent.

Method 2-5.2 CLP-M (cont.)

- 5.6 Recorder: Any multi-range variable speed recorder that is compatible with the UV detection system is suitable.

Note 2: In place of the magnesium perchlorate drying tube, a small reading lamp with 60W bulb may be used to prevent condensation of moisture inside the cell. The lamp is positioned to shine on the absorption cell maintaining the air temperature in the cell about 10°C above ambient.

6. Reagents

- 6.1 Sulfuric Acid, Conc: Reagent grade

6.1.1 Sulfuric acid, 2 N: Dilute 56 ml of conc. sulfuric acid to 1 liter with distilled water.

6.1.2 Sulfuric acid, 10%: Dilute 100 ml conc. sulfuric acid to 1 liter with distilled water.

- 6.2 Nitric acid, Conc: Reagent grade of low mercury content.

6.2.1 Nitric Acid, 0.5% Wash Solution: Dilute 5 ml of concentrated nitric acid to 1 liter with distilled water.

- 6.3 Stannous Sulfate: Add 50 g stannous sulfate to 500 ml of 2 N sulfuric acid (6.1.1). This mixture is a suspension and should be stirred continuously during use.

NOTE 3: Stannous chloride may be used in place of stannous sulfate.

- 6.4 Sodium Chloride-Hydroxylamine Sulfate Solution: Dissolve 30 g of sodium chloride and 30 g of hydroxylamine sulfate in distilled water to 1 liter.

NOTE 4: Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.

- 6.5 Potassium Permanganate: 0.5% solution, w/v. Dissolve 5 g of potassium permanganate in 1 liter of distilled water.

- 6.6 Potassium Permanganate, 0.1 N: Dissolve 3.16 g of potassium permanganate in distilled water and dilute to 1 liter.

- 6.7 Potassium Persulfate: 0.5% solution, w/v. Dissolve 5 g potassium persulfate in 1 liter of distilled water.

- 6.8 Stock Mercury Solution: Dissolve 0.1354 g of mercuric chloride in 75 ml of distilled water. Add 10 ml of conc. nitric acid and adjust the volume to 100.0 ml. 1.0 ml = 1.0 mg Hg.

Method 245.2 CLP-M (cont.)

- 6.9 Working Mercury Solution: Make successive dilutions of the stock mercury solution (6.8) to obtain a working standard containing 0.1 ug per ml. This working standard and the dilutions of the stock mercury solution should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask as needed before the addition of the aliquot. From this solution prepare standards containing 0.2, 0.5, 1.0, 2.0, 5.0, 10.0, 15.0 and 20.0 ug Hg/l.
- 6.10 Air Scrubber Solution: Mix equal volumes of 0.1 N potassium permanganate (6.6) and 10% sulfuric acid (6.1.2).

7. Procedure

- 7.1 Set up manifold as shown in Figure 2.
- 7.2 Feeding all the reagents through the system with acid wash solution (6.2.1) through the sample line, adjust heating bath to 105°C.
- 7.3 Turn on atomic absorption spectrophotometer, adjust instrument settings as recommended by the manufacturer, align absorption cell in light path for maximum transmittance and place heat lamp directly over absorption cell.
- 7.4 Arrange working mercury standards from 0.2 to 20.0 ug Hg/l in sampler and start sampling. Complete loading of sample tray with unknown samples.
- 7.5 Prepare standard curve by plotting peak height of processed standards against concentration values. Determine concentration of samples by comparing sample peak height with standard curve.

NOTE 5: Because of the toxic nature of mercury vapor, precaution must be taken to avoid its inhalation. Venting the mercury vapor into an exhaust hood or passing the vapor through some absorbing media such as:

- a) equal volumes of 0.1 N KMnO_4 (6.6) and 10% H_2SO_4 (6.1.2).
- b) 0.25% iodine in a 3% KI solution, is recommended.

A specially treated charcoal that will adsorb mercury vapor is also available from Barnebey and Cheney, E. 8th Ave. and North Cassidy St., Columbus, Ohio 43219, Cat. #580-13 or #580-22.

- 7.6 After the analysis is complete put all lines except the H_2SO_4 line in distilled water to wash out system. After flushing, wash out the H_2SO_4 line. Also flush the coils in the high temperature heating bath by pumping stannous sulfate (6.3) through the sample lines followed by distilled water. This will prevent build-up of oxides of manganese.

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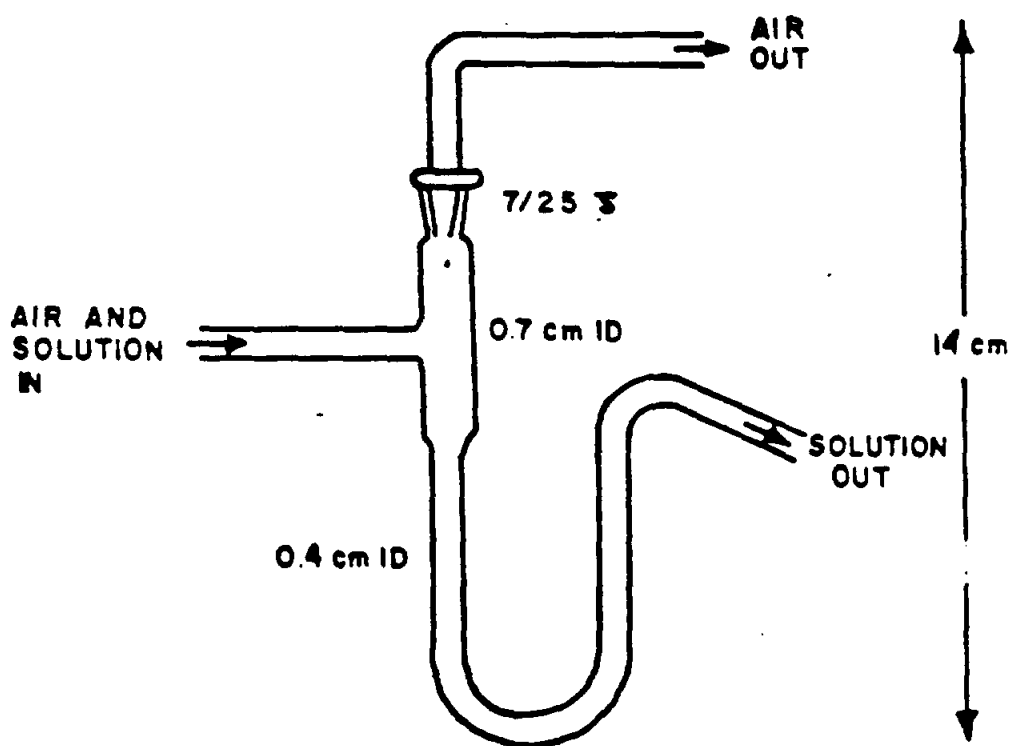


Figure 1. Vapor liquid separator.

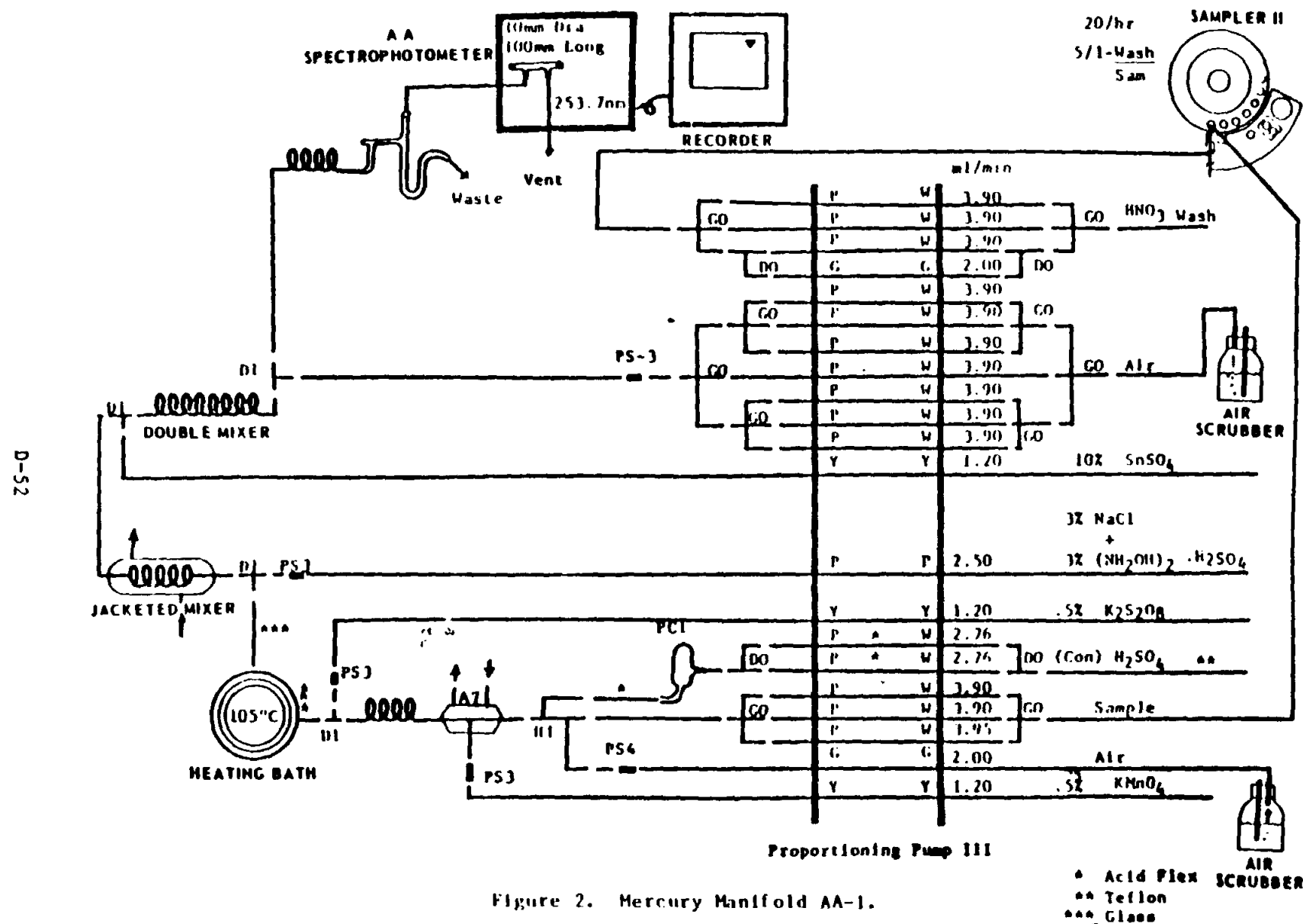


Figure 2. Mercury Manifold AA-1.

ATTACHMENT 6

MERCURY (in Sediments)

Method 245.5 CLP-M* (Manual Cold Vapor Technique)

1. Scope and Application

- 1.1 This procedure measures total mercury (organic and inorganic) in soils, sediments, bottom deposits and sludge type materials.
- 1.2 The range of the method is 0.2 to 5 ug/g. The range may be extended above or below the normal range by increasing or decreasing sample size or through instrument and recorder control.

2. Summary of Method

- 2.1 A weighed portion of the sample is acid digested for 2 minutes at 95°C, followed by oxidation with potassium permanganate and potassium persulfate. Mercury in the digested sample is then measured by the conventional cold vapor technique.
- 2.2 An alternate digestion involving the use of an autoclave is described in (b.2).

3. Sample Handling and Preservation

- 3.1 Because of the extreme sensitivity of the analytical procedure and the omnipresence of mercury, care must be taken to avoid extraneous contamination. Sampling devices and sample containers should be ascertained to be free of mercury; the sample should not be exposed to any condition in the laboratory that may result in contact or air-borne mercury contamination.
- 3.2 Refrigerate solid samples upon receipt.
- 3.3 The sample should be analyzed without drying. A separate % solids determination is required. (Exhibit D, Attachment 9).

4. Interferences

- 4.1 The same types of interferences that may occur in water samples are also possible with sediments, i.e., sulfides, high copper, high chlorides, etc.

*CLP-M modified for the Contract Laboratory Program

Method 245.5 CLP-M (cont.)

- 4.2 Volatile materials which absorb at 253.7 nm will cause a positive interference. In order to remove any interfering volatile materials, purge the dead air space in the BOD bottle before the addition of stannous sulfate.
- 4.3 Sample containing high concentrations of oxidizable organic materials, as evidenced by high chemical oxygen demand values, may not be completely oxidized by this procedure. When this occurs, the recovery of organic mercury will be low. The problem can be eliminated by reducing the weight of the original sample or by increasing the amount of potassium persulfate (and consequently stannous chloride) used in the digestion.

5. Apparatus

- 5.1 Atomic Absorption Spectrophotometer (see Note 1): Any atomic absorption unit having an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed.

NOTE 1: Instruments designed specifically for the measurement of mercury using the cold vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

- 5.2 Mercury Hollow Cathode Lamp: Westinghouse WL-22847, argon filled, or equivalent.
- 5.3 Recorder: Any multi-range variable speed recorder that is compatible with the UV detection system is suitable.
- 5.4 Absorption Cell: Standard spectrophotometer cells 10 cm long, having quartz end windows may be used. Suitable cells may be constructed from pexiglass tubing, 1" O.D. X 4-1/2". The ends are ground perpendicular to the longitudinal axis and quartz windows (1" diameter X 1/16" thickness) are cemented in place. Gas inlet and outlet ports (also of plexiglass but 1/4" O.D.) are attached approximately 1/2" from each end. The cell is strapped to a burner for support and aligned in the light beam to give the maximum transmittance.

NOTE 2: Two 2" X 2" cards with one inch diameter holes may be placed over each end of the cell to assist in positioning the cell for maximum transmittance.
- 5.5 Air Pump: Any peristaltic pump capable of delivering 1 liter of air per minute may be used. A Masterflex pump with electronic speed control has been found to be satisfactory. (Regulated compressed air can be used in an open one-pass system.)
- 5.6 Flowmeter: Capable of measuring an air flow of 1 liter per minute.

Method 245.5 CLP-M (cont.)

- 5.7 **Aeration Tubing:** Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return. Straight glass tubing terminating in a coarse porous frit is used for sparging air into the sample.
- 5.8 **Drying Tube:** 6" X 3/4" diameter tube containing 20 g of magnesium perchlorate (see Note 3). The apparatus is assembled as shown in the accompanying diagram.

NOTE 3: In place of the magnesium perchlorate drying tube, a small reading lamp with 60W bulb may be used to prevent condensation of moisture inside the cell. The lamp is positioned to shine on the absorption cell maintaining the air temperature in the cell about 10°C above ambient.

6. Reagents

- 6.1 **Sulfuric acid, conc.:** Reagent grade of low mercury content.
- 6.2 **Nitric acid, conc.:** Reagent grade of low mercury content.
- 6.3 **Stannous Sulfate:** Add 25 g stannous sulfate to 250 ml of 0.5 N sulfuric acid (6.2). This mixture is a suspension and should be stirred continuously during use.
- 6.4 **Sodium Chloride-Hydroxylamine Sulfate Solution:** Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in distilled water and dilute to 100 ml.
- NOTE 4: A 10% solution of stannous chloride may be substituted for (6.3) and hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate in (6.4).
- 6.5 **Potassium Permanganate:** 5% solution, w/v. Dissolve 5 g of potassium permanganate in 100 ml of distilled water.
- 6.6 **Potassium Persulfate:** 5% solution, w/v. Dissolve 5 g of potassium persulfate in 100 ml of distilled water.
- 6.7 **Stock Mercury Solution:** Dissolve 0.1354 g of mercuric chloride in 75 ml of distilled water. Add ml of conc. nitric acid and adjust the volume to 100.0 ml. 1.0 = 1.0 mg Hg.
- 6.8 **Working Mercury Solution:** Make successive dilutions of the stock mercury solution (6.7) to obtain a working standard containing 0.1 ug/ml. This working standard and the dilution of the stock mercury solutions should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask as needed before the addition of the aliquot.

7. Calibration

- 7.1 Transfer 0, 0.5, 1.0, 5.0 and 10 ml aliquots of the working mercury solutions (6.8) containing 0 to 1.0 ug of mercury to a series of 300 ml BOD bottles. Add enough distilled water to each bottle to make a total volume of 10 ml. Add 5 ml of conc. H_2SO_4 (6.1) and 2.5 ml of conc. HNO_3 (6.2) and heat 2 minutes in a water bath at 95°C. Allow the sample to cool and add 50 ml distilled water, 15 ml of $KMnO_4$ solution (6.5) and 8 ml of potassium persulfate solution (6.6) to each bottle and return to the water bath for 30 minutes. Cool and add 6 ml of sodium chloride-hydroxylamine sulfate solution (6.4) to reduce the excess permanganate. Add 50 ml of distilled water. Treating each bottle individually, add 5 ml of stannous sulfate solution (6.3) and immediately attach the bottle to the aeration apparatus. At this point the sample is allowed to stand quietly without manual agitation. The circulating pump, which has previously been adjusted to a rate of 1 liter per minute, is allowed to run continuously. The absorbance, as exhibited either on the spectrophotometer or the recorder, will increase and reach maximum within 30 seconds. As soon as the recorder pen levels off, approximately 1 minute, open the bypass valve and continue the aeration until the absorbance returns to its minimum value (see Note 5). Close the bypass valve, remove the fritted tubing from the BOD bottle and continue the aeration. Proceed with the standards and construct a standard curve by plotting peak height versus micrograms of mercury.

NOTE 5: Because of the toxic nature of mercury vapor precaution must be taken to avoid its inhalation. Therefore, a bypass has been included in the system to either vent the mercury vapor into an exhaust hood or pass the vapor through some absorbing media, such as:

- a) equal volumes of 0.1 N $KMnO_4$ and 10% H_2SO_4
- b) 0.25% iodine in a 3% KI solution

A specially treated charcoal that will absorb mercury vapor is also available from Barnebey and Cheney, E. 8 Avenue and N. Cassidy Street, Columbus, Ohio 43219

8. Procedure

- 8.1 Weigh a representative 0.2 g portion of wet sample and place in the bottom of a BOD bottle. Add 5 mL of sulfuric acid (6.1) and 2.5 mL of concentrated nitric acid (6.2) mixing after each addition. Heat two minutes in a water bath at 95°C. Cool, add 50 ml distilled water, 15 mL potassium permanganate solution (6.5) and 8 mL of potassium persulfate solution (6.6) to each sample bottle. Mix thoroughly and place in the water bath for 30 minutes at 95°C. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate (6.4) to reduce the excess permanganate. Add 55 mL of distilled water. Treating each bottle individually, add 5 mL of stannous sulfate (6.3) and immediately attach the bottle to the aeration apparatus. Continue as described under (7.1).

Method 245.5 CLP-M (cont.)

- 8.2 An alternate digestion procedure employing an autoclave may also be used. In this method 5 ml of conc. H_2SO_4 and 2 ml of conc. HNO_3 are added to the 0.2 g of sample. 5 ml of saturated $KMnO_4$ solution and 8 ml of potassium persulfate solution are added and the bottle is covered with a piece of aluminum foil. The sample is autoclaved at $121^\circ C$ and 15 lbs. for 15 minutes. Cool, make up to a volume of 100 ml with distilled water and add 6 ml of sodium chloride-hydroxylamine sulfate solution (6.4) to reduce the excess permanganate. Purge the dead air space and continue as described under (8.1).

9. Calculations

- 9.1 Measure the peak height of the unknown from the chart and read the mercury value from the standard curve.
- 9.2 Calculate the mercury concentration in the sample by the formula:
- $$ug\ Hg/g = \frac{ug\ Hg\ in\ the\ aliquot}{wt\ of\ the\ aliquot\ in\ gms\ (based\ upon\ dry\ wt\ of\ the\ sample)}$$
- 9.3 Report mercury concentrations as follows: Below 0.1 ug/gm, 0.1U; between 0.1 and 1 ug/gm, to the nearest 0.01 ug; between 1 and 10 ug/gm, to nearest 0.1 ug; above 10 ug/gm, to nearest ug.

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4. Op. cit. (#3), Methods 245.1 or 245.2.

ATTACHMENT 7

CYANIDE, TOTAL (in Water)

Method 335.2 CLP-M* (Titrimetric; Manual Spectrophotometric;
Semi-Automated Spectrophotometric)

1. Scope and Application

- 1.1 This method is applicable to the determination of cyanide in drinking, surface and saline waters, domestic and industrial wastes.
- 1.2 The titration procedure using silver nitrate with p-dimethylamino-benzalrhodanine indicator is used for measuring concentrations of cyanide exceeding 1 mg/l (0.25 mg/250 ml of absorbing liquid). (Option A)
- 1.3 The manual colorimetric procedure is used for concentrations below 1 mg/l of cyanide and is sensitive to about 0.02 mg/l. (Option B)
- 1.4 The working range of the semi-automated spectrophotometric method is 0.005 to 0.200 mg/l. Higher level samples must be diluted to fall within the working range. (Option C)

2. Summary of Method

- 2.1 The cyanide as hydrocyanic acid (HCN) is released from cyanide complexes by means of a reflux-distillation operation and absorbed in a scrubber containing sodium hydroxide solution. The cyanide ion in the absorbing solution is then determined by volumetric titration or colorimetrically.
- 2.2 In the colorimetric measurement the cyanide is converted to cyanogen chloride, $CNCl$, by reaction with chloramine-T at a pH less than 8 without hydrolyzing to the cyanate. After the reaction is complete, color is formed on the addition of pyridine-pyrazolone or pyridine-barbituric acid reagent. The absorbance is read at 620 nm when using pyridine-pyrazolone or 578 nm for pyridine-barbituric acid. To obtain colors of comparable intensity, it is essential to have the same salt content in both the sample and the standards.
- 2.3 The titimetric measurement uses a standard solution of silver nitrate to titrate cyanide in the presence of a silver sensitive indicator.

*CLP-M Modified for the Contract Laboratory Program

Method 335.2 CLP-M (cont.)

3. Definitions

- 3.1 Cyanide is defined as cyanide ion and complex cyanides converted to hydrocyanic acid (HCN) by reaction in a reflux system of a mineral acid in the presence of magnesium ion.

4. Sample Handling and Preservation

- 4.1 All bottles must be thoroughly cleansed and rinsed to remove soluble material from containers.
- 4.2 Oxidizing agents such as chlorine decompose most of the cyanides. Test a drop of the sample with potassium iodide-starch test paper (KI-starch paper); a blue color indicates the need for treatment. Add ascorbic acid, a few crystals at a time, until a drop of sample produces no color on the indicator paper. Then add an additional 0.6 g of ascorbic acid for each liter of sample volume.
- 4.3 Samples must be preserved with 2 ml of 10 N sodium hydroxide per liter of sample (pH > 12) at the time of collection (see Exhibit F).
- 4.4 Samples should be analyzed as rapidly as possible after collection. The samples must be stored in a refrigerator or in an ice chest filled with water and ice to maintain a temperature of 4°C (see Exhibit F).

5. Interferences

- 5.1 Interferences are eliminated or reduced by using the distillation procedure described in Procedure 8.1.
- 5.2 Sulfides adversely affect the colorimetric and titration procedures. If a drop of the distillate on lead acetate test paper indicates the presence of sulfides, treat 25 ml more of the sample than that required for the cyanide determination with powdered cadmium carbonate. Yellow cadmium sulfide precipitates if the sample contains sulfide. Repeat this operation until a drop of the treated sample solution does not darken the lead acetate test paper. Filter the solution through a dry filter paper into a dry beaker, and from the filtrate measure the sample to be used for analysis. Avoid a large excess of cadmium carbonate and a long contact time in order to minimize a loss by complexation or occlusion of cyanide on the precipitated material. Sulfides should be removed prior to preservation with sodium hydroxide as described in 4.3.
- 5.3 The presence of surfactants may cause the sample to foam during refluxing. If this occurs, the addition of an agent such as Dow Corning 544 antifoam agent will prevent the foam from collecting in the condenser. Fatty acids will distill and form soaps under alkaline titration conditions, making the end point almost impossible to detect. When this occurs, one of the spectrophotometric methods should be used.

Method 335.2 CLP-M (cont.)

6. Apparatus

- 6.1 Reflux distillation apparatus such as shown in Figure 1 or Figure 2. The boiling flask should be of 1 liter size with inlet tube and provision for condenser. The gas absorber may be a Fisher-Milligan scrubber.
- 6.2 Microburet, 5.0 ml (for titration).
- 6.3 Spectrophotometer suitable for measurements at 578 nm or 620 nm with a 1.0 cm cell or larger (for manual spectrophotometric method).
- 6.4 Technicon AA II System or equivalent instrumentation, (for automated spectrophotometric method) including:
 - 6.4.1 Sampler.
 - 6.4.2 Pump III.
 - 6.4.3 Cyanide Manifold (Figure 3).
 - 6.4.4 SCIC Colorimeter with 15 mm flowcells and 570 nm filters.
 - 6.4.5 Recorder.
 - 6.4.6 Data System (optional).
 - 6.4.7 Glass or plastic tubes for the sampler.

7. Reagents

7.1 Distillation and Preparation Reagents

- 7.1.1 Sodium hydroxide solution, 1.25N: Dissolve 50 g of NaOH in distilled water, and dilute to 1 liter with distilled water.
- 7.1.2 Cadmium carbonate: powdered.
- 7.1.3 Ascorbic acid: crystals.
- 7.1.4 Sulfuric acid: concentrated
- 7.1.5 Magnesium chloride solution: Weigh 510 g of $MgCl_2 \cdot 6H_2O$ into a 1000 ml flask, dissolved and dilute to 1 liter with distilled water.

7.2 Stock Standards and Titration Reagents

- 7.2.1 Stock cyanide solution: Dissolve 2.51 g of KCN and 2 g KOH in 1 liter of distilled water. Standardize with 0.0192 N $AgNO_3$.

Method 335.2 CLP-M

- 7.2.2 Standard cyanide solution, intermediate: Dilute 50.0 ml of stock (1 ml = 1 mg CN) to 1000 ml with distilled water (1 ml = 50.0 ug).
- 7.2.3 Standard cyanide solution: Prepare fresh daily by diluting 100.0 ml of intermediate cyanide solution to 1000 ml with distilled water and store in a glass stoppered bottle. 1 ml = 5.0 ug CN (5.0 mg/l).
- 7.2.4 Standard silver nitrate solution, 0.0192 N: Prepare by crushing approximately 5 g AgNO_3 crystals and drying to constant weight at 40°C. Weight out 3.2647 g of dried AgNO_3 , dissolve in distilled water, and dilute to 1000 ml (1 ml = 1 mg CN).
- 7.2.5 Rhodanine indicator: Dissolve 20 mg of p-dimethyl-aminobenzalrhodanine in 100 ml of acetone.
- 7.2.6 Sodium hydroxide solution, 0.25 N: Dissolve 10 g of NaOH in distilled water and dilute to 1 liter.
- 7.3 Manual Spectrophotometric Reagents
 - 7.3.1 Sodium dihydrogenphosphate, 1 M: Dissolve 138 g of $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ in a liter of distilled water. Refrigerate this solution.
 - 7.3.2 Chloramine-T solution: Dissolve 1.0 g of white, water soluble chloramine-T in 100 ml of distilled water and refrigerate until ready to use. Prepare fresh weekly.
 - 7.3.3 Color Reagent - one of the following may be used:
 - 7.3.3.1 Pyridine-barbituric acid reagent: Place 15 g of barbituric acid in a 250 ml volumetric flask and add just enough distilled water to wash the sides of the flask and wet the barbituric acid. Add 75 ml of pyridine and mix. Add 15 ml of HCl (sp gr 1.19), mix, and cool to room temperature. Dilute to 250 ml with distilled water and mix. This reagent is stable for approximately six months if stored in a cool, dark place.
 - 7.3.3.2 Pyridine-pyrazolone solution:
 - 7.3.3.2.1 3-Methyl-1-phenyl-2-pyrazolin-5-one reagent, saturated solution: Add 0.25 g of 3-methyl-1-phenyl-2-pyrazolin-5-one to 50 ml of distilled water, heat to 60°C with stirring. Cool to room temperature.

Method 335.2 CLP-M (cont.)

7.3.3.2.2 3,3'-Dimethyl-1,1'-diphenyl [4,4'-bi-2 pyrazolin]-5,5'-dione (bispyrazolone): Dissolve 0.01 g of bispyrazolone in 10 ml of pyridine.

7.3.3.2.3 Pour solution (7.3.3.2.1) through non-acid-washed filter paper. Collect the filtrate. Through the same filter paper pour solution (7.3.3.2.2) collecting the filtrate in the same container as filtrate from (7.3.3.2.1). Mix until the filtrates are homogeneous. The mixed reagent develops a pink color but this does not affect the color production with cyanide if used within 24 hours of preparation.

7.4 Semi-Automated Spectrophotometric Reagents

7.4.1 Chloramine-T solution: Dissolve 0.40 g of chloramine-T in distilled water and dilute to 100 ml. Prepare fresh daily.

7.4.2 Phosphate buffer: Dissolve 138 g of $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ in distilled water and dilute to 1 liter. Add 0.5 ml of Brij-35 (available from Technicon). Store at 4°C.

7.4.3 Pyridine-barbituric acid solution: Transfer 15 g of barbituric acid into a 1 liter volumetric flask. Add about 100 ml of distilled water and swirl the flask. Add 74 ml of pyridine and mix. Add 15 ml of concentrated HCl and mix. Dilute to about 900 ml with distilled water and mix until the barbituric acid is dissolved. Dilute to 1 liter with distilled water. Store at 4°C.

7.4.4 Sampler wash: Dissolve 10 g of NaOH in distilled water and dilute to 1 liter.

8. Procedure

8.1 Distillation

8.1.1 Place 500 ml of sample, or an aliquot diluted to 500 ml in the 1 liter boiling flask. Add 50 ml of sodium hydroxide (7.1.1) to the absorbing tube and dilute if necessary with distilled water to obtain an adequate depth of liquid in the absorber. Connect the boiling flask, condenser, absorber and trap in the train.

Method 335.2 CLP-M (cont.)

- 8.1.2 Start a slow stream of air entering the boiling flask by adjusting the vacuum source. Adjust the vacuum so that approximately one bubble of air per second enters the boiling flask through the air inlet tube.

CAUTION: The bubble rate will not remain constant after the reagents have been added and while heat is being applied to the flask. It will be necessary to readjust the air rate occasionally to prevent the solution in the boiling flask from backing up into the air inlet tube.

- 8.1.3 Slowly add 25 ml concentrated sulfuric acid (7.1.4) through the air inlet tube. Rinse the tube with distilled water and allow the airflow to mix the flask contents for 3 minutes. Pour 20 ml of magnesium chloride solution (7.1.5) into the air inlet and wash down with a stream of water.
- 8.1.4 Heat the solution to boiling, taking care to prevent the solution from backing up into and overflowing from the air inlet tube. Reflux for one hour. Turn off heat and continue the airflow for at least 15 minutes. After cooling the boiling flask, disconnect absorber and close off the vacuum source.
- 8.1.5 Drain the solution from the absorber into a 250 ml volumetric flask and bring up to volume with distilled water washings from the absorber tube.

8.2 Titrimetric Determination (Option A)

- 8.2.1 If the sample contains more than 1 mg of CN transfer the distillate, or a suitable aliquot diluted to 250 ml, to a 500 ml Erlenmeyer flask. Add 10-12 drops of the benzal-rhodanine indicator.
- 8.2.2 Titrate with standard silver nitrate to the first change in color from yellow to brownish-pink. Titrate a distilled water blank using the same amount of sodium hydroxide and indicator as in the sample.
- 8.2.3 The analyst should familiarize himself with the end point of the titration and the amount of indicator to be used before actually titrating the samples. A 5 or 10 ml microburet may be conveniently used to obtain a more precise titration.

8.3 Manual Spectrophotometric Determination (Option B)

8.3.1 Withdraw 50 ml or less of the solution from the flask and transfer to a 100 ml volumetric flask. If less than 50 ml is taken, dilute to 50 ml with 0.25 N sodium hydroxide solution (7.2.6). Add 15.0 ml of sodium phosphate solution (7.3.1) and mix.

8.3.1.1 Pyridine-barbituric acid method: Add 2 ml of chloramine-T (7.3.2) and mix. After 1 to 2 minutes, add 5 ml of pyridine-barbituric acid solution (7.3.3.1) and mix. Dilute to mark with distilled water and mix again. Allow 8 minutes for color development then read absorbance at 578 nm in a 1 cm cell within 15 minutes.

8.3.1.2 Pyridine-pyrazolone method: Add 0.5 ml of chloramine-T (7.3.2) and mix. After 1 to 2 minutes, add 5 ml of pyridine-pyrazolone solution (7.3.3.2) and mix. Dilute to mark with distilled water and mix again. After 40 minutes, read absorbance at 620 nm in a 1 cm cell.

NOTE: More than 0.5 of chloramine-T will prevent the color from developing with pyridine-pyrazolone.

8.3.2 Prepare a minimum of 3 standards and a blank by pipeting suitable volumes of standard solution into 250 ml volumetric flasks. NOTE: One calibration standard must be at the CRDL. To each standard add 50 ml of 1.25 N sodium hydroxide and dilute to 250 ml with distilled water. Standards must bracket the concentration of the samples. If dilution is required, use the blank solution. As an example, standard solutions could be prepared as follows:

<u>ml of Standard Solution</u> <u>(1.0 = 5 ug CN)</u>	<u>Conc. ug CN</u> <u>per 250 ml</u>
0	Blank
1.0	5
2.0	10
5.0	25
10.0	50
15.0	60
20.0	100

8.3.2.1 It is not imperative that all standards be distilled in the same manner as the samples. At least one standard (mid range) must be distilled and compared to similar values on the curve to insure that the distillation technique is reliable. If the distilled standard does not agree within +15% of the undistilled standards, the operator should find and correct the cause of the apparent error before proceeding.

Method 335.2 CLP-H (cont.)

8.3.2.2 Prepare a standard curve by plotting absorbance of standard vs. cyanide concentrations (per 250 ml).

8.4 Semi-Automated Spectrophotometric Determination (Option C)

8.4.1 Set up the manifold as shown in Figure 3. Pump the reagents through the system until a steady baseline is obtained.

8.4.2 Calibration standards: Prepare a blank and at least three calibration standards over the range of the analysis. One calibration standard must be at the CRDL. For a working range of 0-200 ug/l, the following standards may be used:

<u>ml Standard Solution</u> <u>(7.2.3) diluted to 1 liter</u>	<u>Concentration</u> <u>ug CN/l</u>
0	0
4.0	20
10.0	50
20.0	100
30.0	150
40.0	200

Add 10 g of NaOH to each standard. Store at 4°C.

8.4.3 Place calibration standards, blanks, and control standards in the sampler tray, followed by distilled samples, distilled duplicates, distilled standards, distilled spikes, and distilled blanks.

8.4.4 When steady reagent baseline is obtained, and before starting the sampler, adjust the baseline using the appropriate knob on the colorimeter. Aspirate a calibration standard and adjust the STD CAL dial on the colorimeter until the desired signal is obtained. Record the STD CAL value. Re-establish the baseline and proceed to analyze calibration standards, blanks, control standards, distilled samples, and distilled QC audits.

9. CALCULATIONS

9.1 Using the titrimetric procedure, calculate concentration of CN as follows:

$$\text{CN, mg/l} = \frac{(A - B) 1,000 \frac{\text{ml}}{\text{l}}}{\text{ml orig. sample}} \times \frac{250 \text{ ml}}{\text{ml of aliquot titrated}}$$

WHERE: A = volume of AgNO₃ for titration of sample (1 ml = 1 mg Ag)

B = volume of AgNO₃ for titration of blank (1 ml = 1 mg Ag)

Method 335.2 CLP-M (cont.)

And: 250 ml = distillate volume (See 8.1.5)
1000 ml = conversion ml to L
ml original sample (See 8.1.1)
ml of aliquot titrated (See 8.2.1)

- 9.2 If the colorimetric procedure is used, calculate the cyanide, in ug/l, in the original sample as follows:

$$\text{CN, ug/l} = \frac{A \times 1,000}{B} \times \frac{50 \text{ ml}}{C}$$

WHERE: A = ug CN read from standard curve (per 250 mL)
B = ml of original sample for distillation (See 8.1.1)
C = ml taken for colorimetric analysis (See 8.3.1)

AND: 50 ml = volume of original sample aliquot (See 8.3.1)
 $\frac{1000 \text{ ml}}{1}$ = conversion ml to L

- 9.3 If the semi-automated method is used, measure the peak heights of the calibration standards (visually or using a data system) and calculate a linear regression equation. Apply the equation to the samples and QC audits to determine the cyanide concentration in the distillates. To determine the concentration of cyanide in the original sample MULTIPLY THE RESULTS BY ONE-HALF (since the original volume was 500 ml and the distillate volume was 250 ml). Also, correct for any dilutions which were made before or after distillation.

10. Bibliography

1. Methods for "Chemical Analysis of Water and Wastes", March 1979, EPA publication #600/4-79-02.
2. "Operation Manual for Technicon Auto Analyzer IIC System", 1980. Technical publication #TA9-0460-00. Technicon Industrial Systems, Tarrytown, NY, 10591.
3. "Users Guide for the Continuous Flow Analyzer Automation System", EMSL U.S. EPA, Cincinnati, OH (1981).
4. Interim Methods for the Sampling and Analysis of Priority Pollutants in Sediments and Fish Tissue," USEPA Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, August 1977, Revised October 1980.
5. Op. cit. (#4), Methods 335.2.

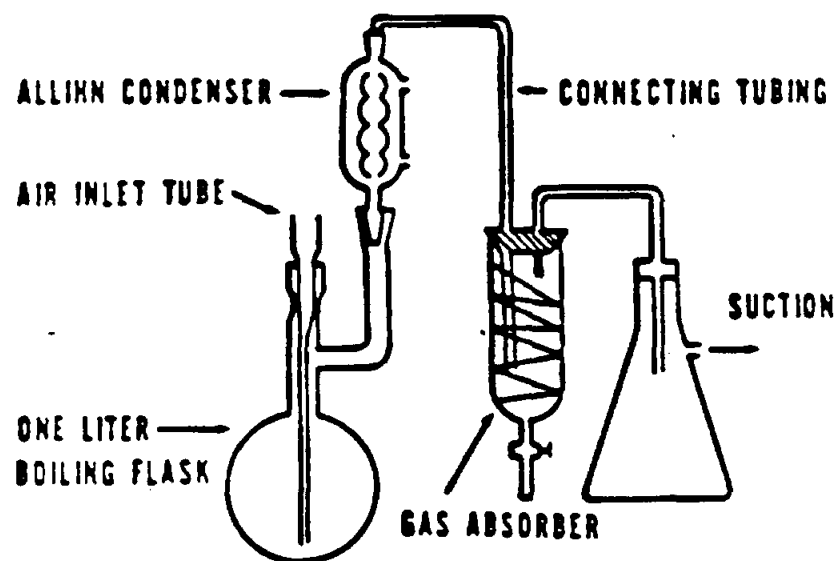


Figure 1. Cyanide distillation apparatus.

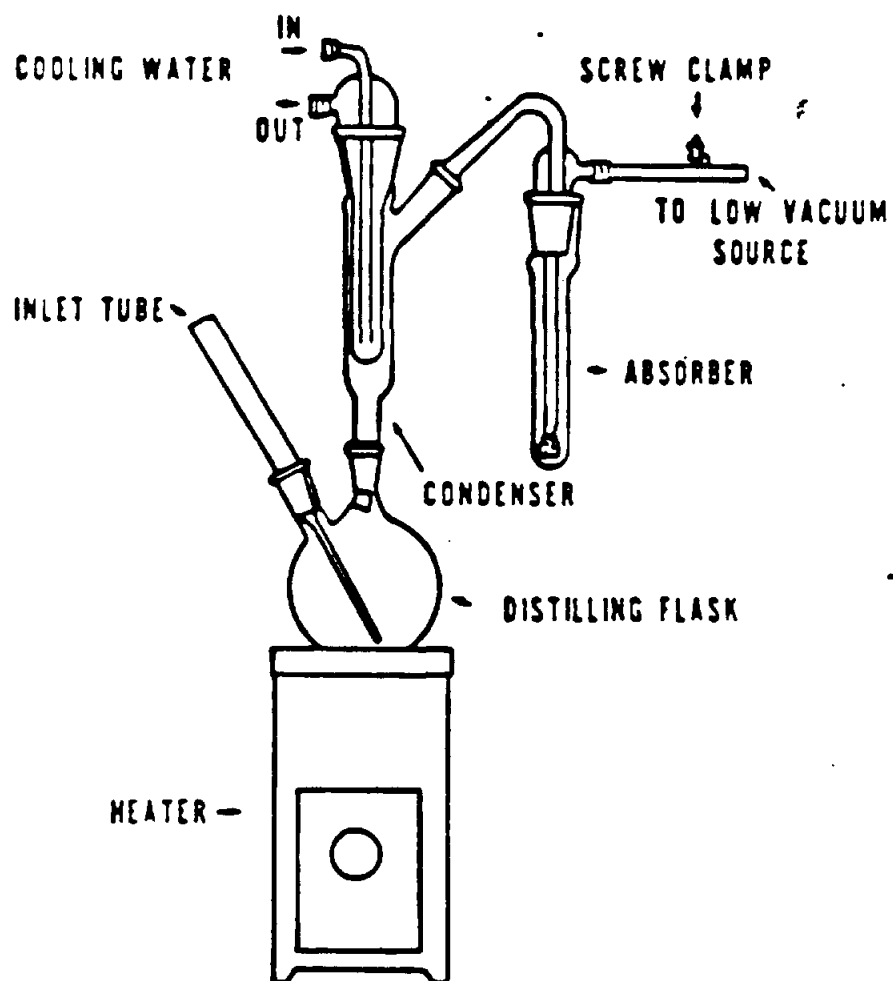


Figure 2. Cyanide distillation apparatus.

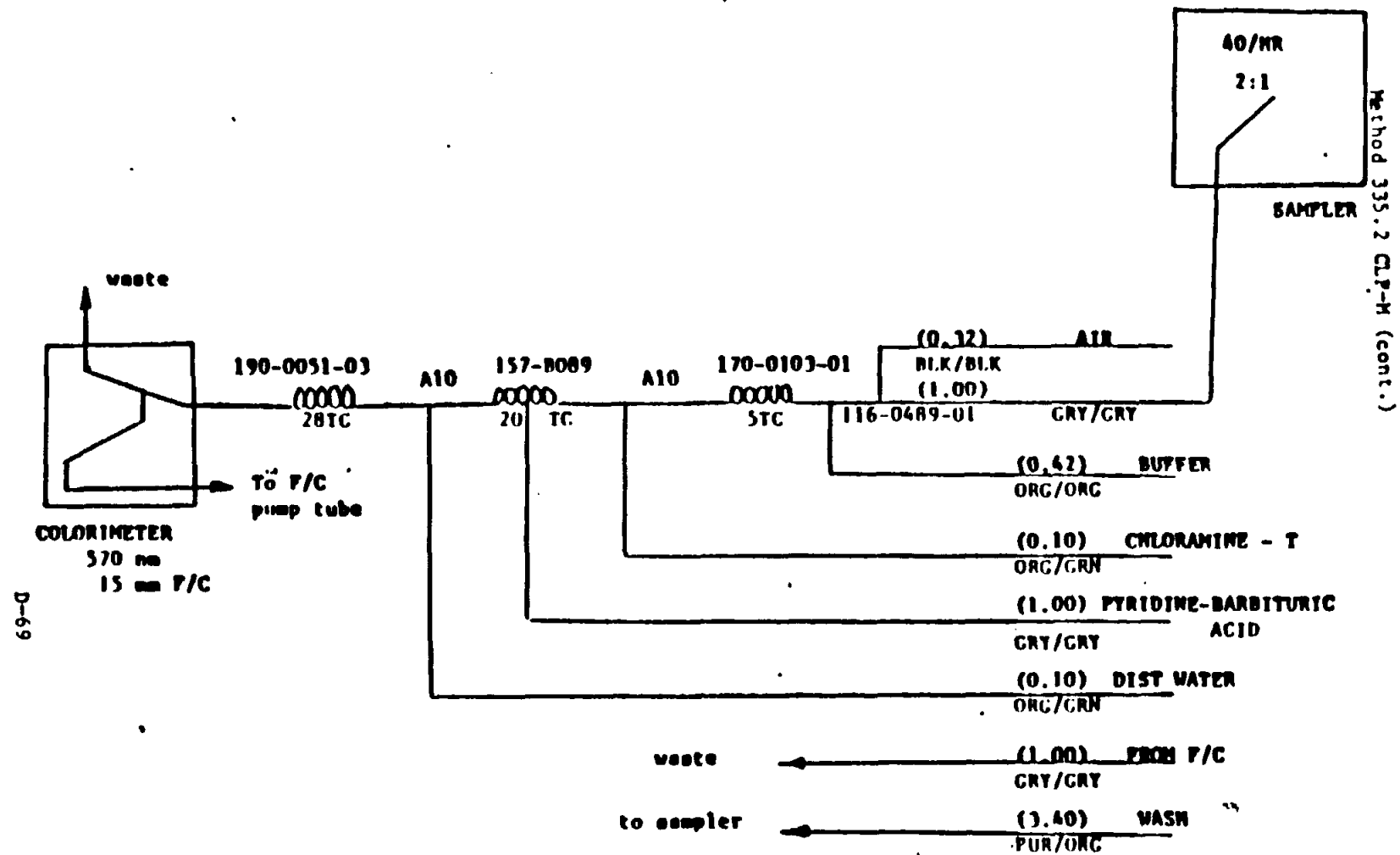


Figure 3. Cyanide manifold.

ATTACHMENT 8

CYANIDE, TOTAL (in Sediments)

Method 335.2 CLP-M* (Titrimetric; Manual Spectrophotometric;
Semi-Automated Spectrophotometric)

1. Scope and Application

- 1.1 This method is applicable to the determination of cyanide in sediments and other solids.
- 1.2 The detection limit is dependent upon the weight of sample taken for analysis.

2. Summary of Method

- 2.1 The cyanide as hydrocyanic acid (HCN) is released from cyanide complexes by means of a reflux-distillation operation and absorbed in a scrubber containing sodium hydroxide solution. The cyanide ion in the absorbing solution is then determined by volumetric titration or colorimetrically.
- 2.2 In the colorimetric measurement the cyanide is converted to cyanogen chloride, $CNCl$, by reaction with chloramine-T at a pH less than 8 without hydrolyzing to the cyanate. After the reaction is complete, color is formed on the addition of pyridine-pyrazolone or pyridine-barbituric acid reagent. The absorbance is read at 620 nm when using pyridine-pyrazolone for 578 nm for pyridine-barbituric acid. To obtain colors of comparable intensity, it is essential to have the same salt content in both the sample and the standards.
- 2.3 The titrimetric measurement uses a standard solution of silver nitrate to titrate cyanide in the presence of a silver sensitive indicator.

3. Definitions

- 3.1 Cyanide is defined as cyanide ion and complex cyanides converted to hydrocyanic acid (HCN) by reaction in a reflux system of a mineral acid in the presence of magnesium ion.

*CLP-M Modified for the Contract Laboratory Program

Method 335.2 (Sed.) CLP-M (cont.)

4. Sample Handling and Preservation

- 4.1 Samples are stored at 4°C. No holding times have been established.
- 4.2 Samples are not dried prior to analysis. A separate % solids determination must be made (see Exhibit D, Attachment 9).

5. Interferences

- 5.1 Interferences are eliminated or reduced by using the distillation procedure described in Procedure 8.1.
- 5.2 Sulfides adversely affect the colorimetric and titration procedures.
- 5.3 The presence of surfactants may cause the sample to foam during refluxing. If this occurs, the addition of an agent such as DOW Corning 544 antifoam agent will prevent the foam from collecting in the condenser. Fatty acids will distill and form soaps under the alkaline titration conditions, making the end point almost impossible to detect. When this occurs, one of the spectrophotometric methods should be used.

6. Apparatus

- 6.1 Reflux distillation apparatus such as shown in Figure 1 or Figure 2. The boiling flask should be of 1 liter size with inlet tube and provision for condenser. The gas absorber may be a Fisher-Milligan scrubber.
- 6.2 Microburet, 5.0 ml (for titration)
- 6.3 Spectrophotometer suitable for measurements at 576 nm or 620 nm with a 1.0 cm cell or larger.
- 6.4 Technicon AA II System (for automated spectrophotometric method) including:
 - 6.4.1 Sampler
 - 6.4.2 Pump III
 - 6.4.3 Cyanide Manifold (Figure 3)
 - 6.4.4 SCIC Colorimeter with 15 mm flowcells and 570 nm filters
 - 6.4.5 Recorder
 - 6.4.6 Data System (optional)
 - 6.4.7 Glass or plastic tubes for the sampler

7. Reagents

7.1 Distillation and Preparation Reagents

- 7.1.1 Sodium hydroxide solution, 1.25N: Dissolve 50 g of NaOH in distilled water, and dilute to 1 liter with distilled water.
- 7.1.2 Cadmium carbonate: powdered
- 7.1.3 Ascorbic acid: crystals
- 7.1.4 Sulfuric acid: concentrated
- 7.1.5 Magnesium chloride solution: Weigh 510 g of $MgCl_2 \cdot 6H_2O$ into a 1000 ml flask, dissolve and dilute to 1 liter with distilled water.

7.2 Stock Standards and Titration Reagents

- 7.2.1 Stock cyanide solution: Dissolve 2.51 g of KCN and 2 g KOH in 1 liter of distilled water. Standardize with 0.0192 N $AgNO_3$.
- 7.2.2 Standard cyanide solution, intermediate: Dilute 50.0 ml of stock (1 ml = 1 mg CN) to 1000 ml with distilled water (1 ml = 50.0 ug).
- 7.2.3 Standard cyanide solution: Prepare fresh daily by diluting 100.0 ml of intermediate cyanide solution to 1000 ml with distilled water and store in a glass stoppered bottle. 1 ml = 5.0 ug CN (5.0 mg/l).
- 7.2.4 Standard silver nitrate solution, 0.0192 N: Prepare by crushing approximately 5 g $AgNO_3$ crystals and drying to constant weight at 40°C. Weigh out 3.2647 g of dried $AgNO_3$, dissolve in distilled water, and dilute to 1000 ml (1 ml = 1 mg CN).
- 7.2.5 Rhodanine indicator: Dissolve 20 mg of p-dimethyl-amino-benzalrhodanine in 100 ml acetone.

7.3 Manual Spectrophotometric Reagents

- 7.3.1 Sodium dihydrogenphosphate, 1 M: Dissolve 138 g of $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ in 1 liter of distilled water. Refrigerate this solution.
- 7.3.2 Chloramine-T solution: Dissolve 1.0 g of white, water soluble Chloramine-T in 100 ml of distilled water and refrigerate until ready to use. Prepare fresh weekly.
- 7.3.3 Color reagent - One of the following may be used:
- 7.3.3.1 Pyridine-barbituric acid reagent: Place 15 g of barbituric acid in a 250 ml volumetric flask and add just enough distilled water to wash the sides of the flask and wet the barbituric acid. Add 75 ml of pyridine and mix. Add 15 ml of HCl (sp gr 1.19), mix, and cool to room temperature. Dilute to 250 ml with distilled water and mix. This reagent is stable for approximately six months if stored in a cool, dark place.
- 7.3.3.2 Pyridine-pyrazolone solution:
- 7.3.3.2.1 3-Methyl-1-phenyl-2-pyrazolin-5-one reagent, saturated solution: Add 0.25 g of 3-methyl-1-phenyl-2-pyrazolin-5-one to 50 ml of distilled water, heat to 60°C with stirring. Cool to room temperature.
- 7.3.3.2.2 3,3'-Dimethyl-1,1'-diphenyl-[4,4'-bi-2-pyrazolin]-5,5'-dione (bispyrazolone): Dissolve 0.01 g of bispyrazolone in 10 ml of pyridine.
- 7.3.3.2.3 Pour solution (7.3.3.2.1) through non-acid-washed filter paper. Collect the filtrate. Through the same filter paper pour solution (7.3.3.2.2) collecting the filtrate in the same container as filtrate from (7.3.3.2.1). Mix until the filtrates are homogeneous. The mixed reagent develops a pink color but this does not affect the color production with cyanide if used within 24 hours of preparation.

7.4 Semi-Automated Spectrophotometric Reagents

- 7.4.1 Chloramine-T solution: Dissolve 0.40 g of chloramine-T in distilled water and dilute to 100 ml. Prepare fresh daily.
- 7.4.2 Phosphate Buffer: Dissolve 138 g of $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ in distilled water and dilute to 1 liter. Add 0.5 ml of Brij-35 (available from Technicon). Store at 4°C.
- 7.4.3 Pyridine-barbituric acid solution: Transfer 15 g of barbituric acid into a 1 liter volumetric flask. Add about 100 ml of distilled water and swirl the flask. Add 74 ml of pyridine and mix. Add 15 ml of conc. HCl mix until the barbituric acid is dissolved. Dilute to 1 liter with distilled water. Store at 4°C.
- 7.4.4 Sampler Wash: Dissolve 10 g of NaOH in distilled water and dilute to 1 liter.

8. Procedure

8.1 Distillation

- 8.1.1 Accurately weigh a representative 1-5 g portion of wet sample and transfer it to a boiling flask. Add 500 ml of distilled water. Shake or stir the sample so that it is dispersed.
- 8.1.2 Add 50 ml of sodium hydroxide (7.1.1) to the absorbing tube and dilute if necessary with distilled water to obtain an adequate depth of liquid in the absorber. Connect the boiling flask, condenser, absorber, and trap in the train.
- 8.1.3 Start a slow stream of air entering the boiling flask by adjusting the vacuum source. Adjust the vacuum so that approximately one bubble of air per second enters the boiling flask through the air inlet tube.

CAUTION: The bubble rate will not remain constant after the reagents have been added and while heat is being applied to the flask. It will be necessary to readjust the air rate occasionally to prevent the solution in the boiling flask from backing up into the air inlet tube.

- 8.1.4 Slowly add 25 ml of conc. sulfuric acid (7.1.4) through the air inlet tube. Rinse the tube with distilled water and allow the airflow to mix the flask contents for 3 minutes. Pour 20 ml of magnesium chloride solution (7.1.5) into the air inlet and wash down with a stream of water.

Method 335.2 (Sed.) CLP-M (cont.)

3.14 CORRECTIVE ACTION

8.1.5 Heat the solution to boiling, taking care to prevent the solution from backing up and overflowing into the air inlet tube. Reflux for one hour. Turn off heat and continue the airflow for at least 15 minutes. If the periodic quality control audits detect unacceptable boiling the boiling flask, disconnect absorber and close off the vacuum source.

If the periodic conditions or data, the G&M Project Director, G&M QA/QC Officer,

8.1.6 Drain the solution from the absorber into a 250 ml volumetric flask and wash up to volume with distilled water and G&M Project Manager are responsible for developing and initiating appropriate changes or modifications. The condition

8.2 Titrimetric Determination (Option A)
 or problem will be specifically identified, recorded in the

8.2.1 If the sample contains more than 1 mg of CN transfer the appropriate field log or project file. Investigate, and 50 ml, to a 900 ml Erlenmeyer flask. Add 10-12 drops of the benzalrhodanine indicator.

cause determined. Then, changes or modifications will be initiated to eliminate the problem. These may include:
 8.2.2 Titrate with standard silver nitrate to the first change in color from colorless to brownish pink. Titrate a distilled water blank using the same amount of sodium hydroxide and indicator as in the sample.

- Re-analyzing samples if the end point of the titration and the amount of indicator to be used before actually titrating the samples. A 5 or 10 ml microburet may be conveniently used to obtain a more precise titration.

8.3 Manual Spectrophotometric Determination (Option B)

- Resampling and re-analyzing less of the solution from the flask and transfer to a 100 ml volumetric flask. If less than 50 ml is taken, dilute to 50 ml with 0.25 N sodium hydroxide solution (7.2.6). Add 15.0 ml of sodium phosphate solution (7.3.2) and mix.
- Evaluating and amending sampling and/or analytical procedures,

- 8.3.1.1 Pyridine-barbituric acid method: Add 2 ml of Chloramine-T (7.3.2) and mix. After 1 to 2 minutes, add 5 ml of pyridine-barbituric acid solution (7.3.3.1) and mix. Dilute to mark with distilled water and mix again. Allow 8 minutes. Accepting data, while documenting a level of uncertainty. For color development then read absorbance at 578 nm in a 1 cm cell within 15 minutes.

8.3.1.2 Pyridine-pyrazolone method: Add 0.5 ml of Chloramine-T (7.3.2) and mix. After 1 to 2 minutes, add 5 ml of pyridine-pyrazolone solution (7.3.3.2) and mix. Dilute to mark with distilled water and mix again. After 40 minutes read absorbance at 620 nm in a 1 cm cell. Upon implementation of changes or modifications, their effectiveness will be established and elimination of the problem verified. Details regarding the changes or modifications implemented and the results will be documented and retained in the project file.

NOTE: More than 0.5 ml of chloramine-T will prevent the color from developing with pyridine-pyrazolone.

- 8.3.2 Prepare a minimum of three of standards and a blank by pipetting suitable volumes of standard solution into 250 ml volumetric flasks. One calibration standard must be made at the CRDL. To each standard add 50 ml of 1.25 N sodium hydroxide and dilute to 250 ml with distilled water. Standards must bracket the concentrations of the sample. If dilution is required, use the blank solution. As an example, standard solutions could be prepared as follows:

<u>ml of Standard Solution</u> <u>(1.0 = 5 ug CN)</u>	<u>Conc. ug CN</u> <u>per 250 ml</u>
0	Blank
1.0	5
2.0	10
5.0	25
10.0	50
15.0	60
20.0	100

- 8.3.2.1 It is not imperative that all standards be distilled in the same manner as the samples. At least one standard (mid range) must be distilled and compared to similar values on the curve to insure that the distillation technique is reliable. If the distilled standard does not agree within +15% of the undistilled standards the operator should find and correct the cause of the apparent error before proceeding.

- 8.3.2.2 Prep a standard curve by plotting absorbance of stand. A vs. cyanide concentrations (per 250 mL)

8.4 Semi-Automated Spectrophotometric Determination (Option C)

- 8.4.1 Set up the manifold as shown in Figure 3. Pump the reagents through the system until a steady baseline is obtained.
- 8.4.2 Calibration standards: Prepare a blank and at least three calibration standards over the range of the analysis. One calibration standard must be at the CRDL. For a working range of 0-200 ug/l, the following standards may be used:

Method 335.2 (Sed.) CLP-M (cont.)

3.15 QA REPORTS TO MANAGEMENT

ml Standard Solution (7.2.3) diluted to 1 liter	Concentration ug CN/l
--	--------------------------

On a regular basis, the G&M QA/QC Officer will review all aspects of the implementation of this QAPP and prepare a summary report to the G&M Project Manager and G&M Project Director.

Reviews will be performed at the completion of each field activity and reports will be completed at this time. Add 10 g of NaOH to each standard for storage at 4°C.

8.4.3 Place calibration standards, blanks, and control standards activity and reports will be completed at this time. These distilled duplicates, distilled standards, distilled spikes, reports will include: and distilled blanks.

- 8.4.4 When a steady reagent baseline is obtained, and before starting the sampler, adjust the baseline using the appropriate knob on the colorimetry system. Calibration standard and adjust the STD CAL dial on the colorimeter until the desired signal is obtained. Record the STD CAL value. Reestablish the baseline and proceed to analyze calibration standards, blanks, control standards, distilled samples, and distilled QC audits.

- 8 Results of performance, systems, data, and instrument

9.1 A separate determination of % solids must be performed (see Exhibit D, Attachment 9).

- 9.2 The concentration of cyanide in the sample is determined as follows.
- Any changes or modifications which need to be taken or

are to be taken.

$$\text{CN, mg/kg} = \frac{(A - B) \times \frac{250 \text{ ml}}{\text{ml aliquot titrated}} \times 1000 \text{ g/kg}}{C \times \frac{\% \text{ solids}}{100}}$$

Any significant QA problems will be reported and identified, and options for changing or modifying the program can be discussed.

AND: 250 ml = volume of distillate (See 8.1.6)
1000 g/kg = conversion factor g to kg
ml aliquot titrated (See 8.2.1)
% solids (See attachment 9)

Method 335.2 (Sed.) CLP-M (cont.)

9.2.2 (Manual Spectrophotometric)

$$\text{CN, mg/kg} = \frac{A \times \frac{50 \text{ ml}}{B}}{C \times \frac{\% \text{ solids}}{100}}$$

Where: A = ug CN read from standard curve (per 250 mL)
B = ml of distillate taken for colorimetric determination (8.3.1)
C = wet weight of original sample in g (See 8.1.1)

And: 50 ml = volume of standard taken for colorimetric determination (See 8.3.1)
% solids (See attachment 9)

9.2.3 (Semi-Automated Spectrophotometric)

If the semi-automated method is used, measure the peak heights of the calibration standards (visually or using a data system) and calculate a linear regression equation. Apply the equation to the samples and QC audits to determine the cyanide concentration in the distillates.

$$\text{CN, ng/kg} = \frac{A \times .25}{C \times \frac{\% \text{ solids}}{100}}$$

Where: A = ug/l determined from standard curve
C = wet weight of original sample in g (See 8.1.1)

And: .25 = conversion factor for distillate final volume (See 8.1.6)
% solids (See attachment 9)

10. Bibliography

1. Modification of Method 335.2: Cyanide, Total
2. Methods for "Chemical Analysis of Water and Wastes", March 1979. EPA Publication #600/4-79-02.
3. "Operation Manual for Technicon Auto Analyzer IIC System", 1980. Technical publication #TA9-0460-00. Technicon Industrial Systems, Tarrytown, NY, 10591.
4. "Users Guide for the Continuous Flow Analyzer Automation System", ESL, U.S. EPA, Cincinnati, Ohio (1981).
5. "Interim Methods for the Sampling and Analysis of Priority Pollutants in Sediments and Fish Tissue," USEPA Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, August 1977, Revised October 1980.
6. Op. cit. (#5), Methods 335.2, modified (by committee).

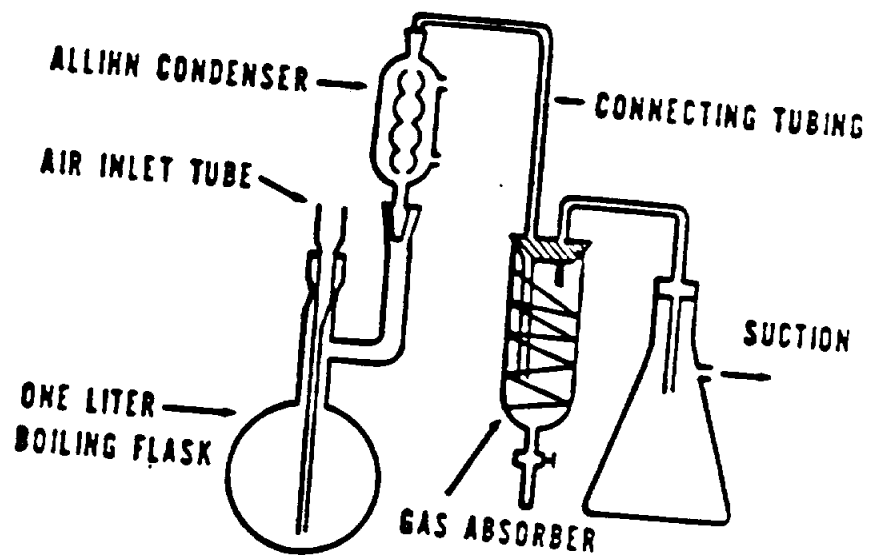


Figure 1. Cyanide distillation apparatus.

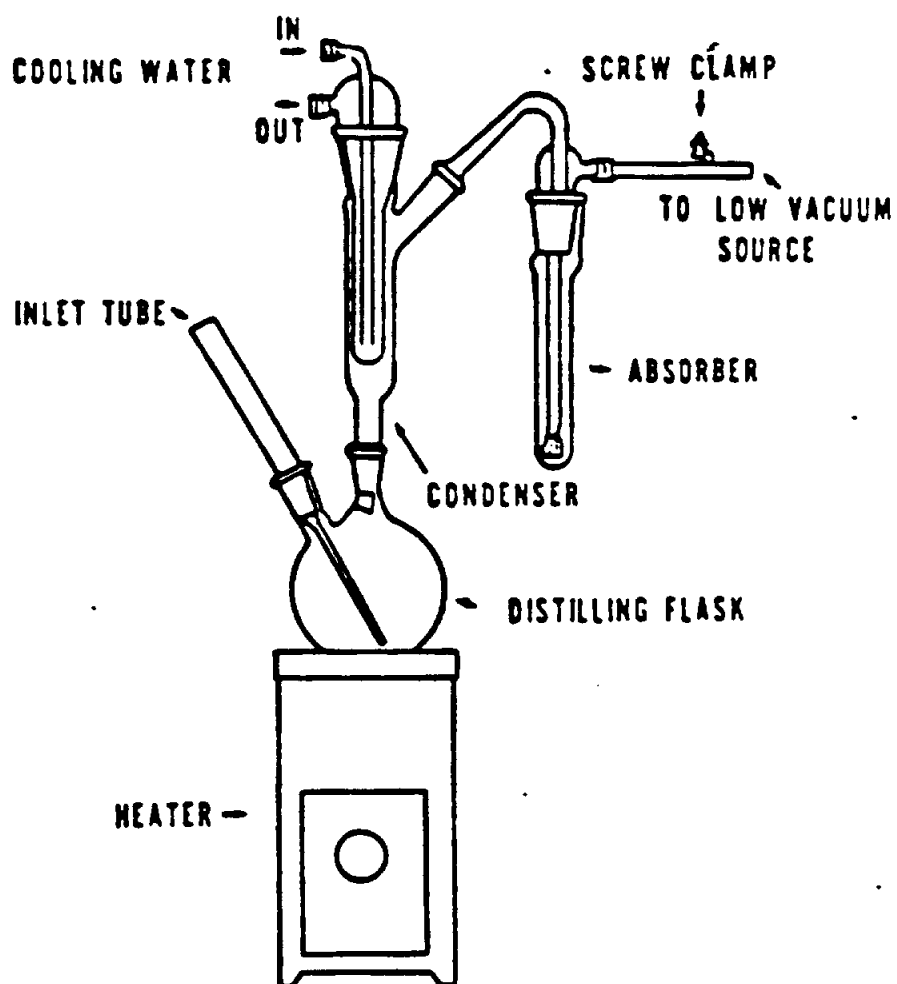


Figure 2. Cyanide distillation apparatus.

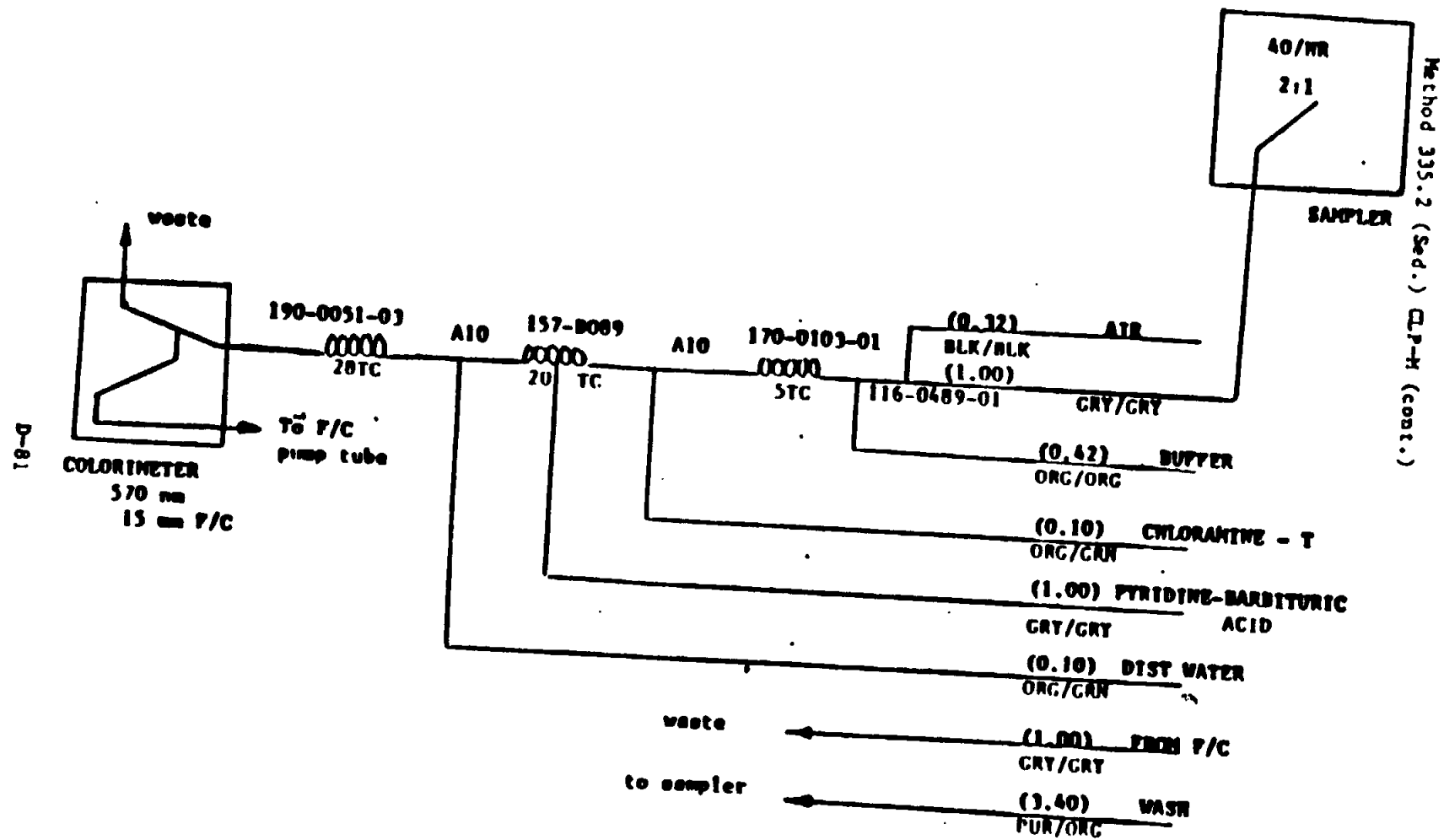


Figure 3. Cyanide Manifold.

ATTACHMENT 9

PERCENT (%) SOLIDS

1. Immediately following the weighing of the sample to be processed for analysis (see Attachment 1), add 5-10 g. of sample to a tared weighing dish. Weigh and record the weight to the nearest 0.001 g.
2. Place weighing dish plus sample, with the cover tipped to allow for moisture escape, in a drying oven that is set at 103-105° C. Sample handling and drying should be conducted in a well ventilated area.
3. Dry the sample overnight (12-24 hours) but no longer than 24 hours. If dried less than 12 hours, it must be documented that constant weight was attained.* Remove the sample from the oven and cool in a dessicator with the weighing dish cover in place before weighing. Weigh and record weight to nearest 0.001 g. Do not analyze the dried sample.
4. Duplicate % solids determinations are required at the same frequency as are other analytical determinations. Duplicate results are to be recorded on Form VI as well as on the appropriate Form I's. (See Duplicates, Exhibit E).
5. For the duplicate % solids determination, designate one sample aliquot as the "original" sample and the other aliquot as the "duplicate" sample. Perform all Form I calculations for that EPA sample using the results of the "original" sample aliquot. Where the same EPA sample is selected for duplication of % solids as was selected for the analytical duplicate, the % solids result for the "duplicate" aliquot will be used for the Form I calculations for the EPA sample analytical duplicate.
6. Calculate % solids by the formula below. The value thus obtained will be reported on the appropriate Form I and, where applicable, Form VI. This value will be used for calculating analytical concentration on a dry weight basis in accordance with the appropriate equation in Attachments 1, 6, and 8.

$$\% \text{ Solids} = \frac{\text{Sample Dry Weight}}{\text{Sample Wet Weight}} \times 100$$

*For the purpose of paragraph 3, drying time is defined as the elapsed time in the oven; thus raw data must record time in and out of the oven to document the 12 hour drying time minimum. In the event it is necessary to demonstrate the attainment of constant weight, data must be recorded for a minimum of two repetitive weigh/dry/dessicate/weigh cycles with a minimum of 1 hour drying time in each cycle. Constant weight would be defined as a loss in weight of no greater than 0.001 g between the start weight and final weight of the last cycle.

ATTACHMENT 10

Alternate Methods (Catastrophic ICP Failure)

The methods contained in this attachment may be used only if all of the following conditions are met:

- 1) Catastrophic failure of ICP occurs,
- 2) Project Officer authorization for use of alternate methods is granted, and
- 3) The IDLs for the instrumentation have been determined, as per Exhibit E, within the previous 30 days.

ALUMINUM*

Method 202.2 CLP-M**(Atomic Absorption, furnace technique)

Optimum Concentration Range: 20-200 ug/l

Approximate Detection Limit: 3 ug/l

Preparation of Standard Solution

1. Stock solution: Prepare as described under "direct aspiration method" (Exhibit D, Attachment 4).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".
3. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec-125°C.
2. Ashing Time and Temp: 30 sec-1300°C.
3. Atomizing Time and Temp: 10 sec-2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 309.3 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 ul injection, continuous flow purge gas and non-pyrolytic graphite and are to be used as guidelines only.
2. Background correction is required.
3. It has been reported that chloride ion and that nitrogen used as a purge gas suppress the aluminum signal. Therefore the use of halide acids and nitrogen as a purge gas should be avoided.
4. For every sample analyzed, verification is necessary to determine that method of standard addition is not required (Exhibit E).
5. If method of standard addition is required, follow the procedure given in Exhibit E.

*This method may only be used under certain conditions (see D-83)

**CLP-M Modified for the Contract Laboratory Program

BARIUM*

Method 208.2 CLP-M (Atomic Absorption, furnace technique)

Optimum Concentration Range: 10-200 ug/l
Approximate Detection Limit: 2 ug/l

Preparation of Standard Solution

1. Stock solution: Prepare as described under "direct aspiration method" (Exhibit D, Attachment 4).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".
3. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec-125°C.
2. Ashing Time and Temp: 30 sec-1200°C.
3. Atomizing Time and Temp: 10 sec-2800°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 553.6 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 ul injection, continuous flow purge gas and pyrolytic graphite and are to be used as guidelines only.
2. The use of halide acid should be avoided.
3. Because of possible chemical interaction, nitrogen should not be used as a purge gas.
4. For every sample analyzed, verification is necessary to determine that method of standard addition is not required (see Exhibit E).
5. If method of standard addition is required, follow the procedure given in Exhibit E.

*This method may only be used under certain conditions (see D-83)

COBALT*

Method 219.2 CLP-M (Atomic Absorption, furnace technique)

Optimum Concentration Range: 5-100 ug/l
Approximate Detection Limit: 1 ug/l

Preparation of Standard Solution

1. Stock solution: Prepare as described under "direct aspiration method" (Exhibit D, Attachment 4).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".
3. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec-125°C.
2. Ashing Time and Temp: 30 sec-900°C.
3. Atomizing Time and Temp: 10 sec-2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 240.7 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 ul injection, continuous flow purge gas and non-pyrolytic graphite and are to be used as guidelines only. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is required.
3. Nitrogen may also be used as the purge gas but with reported low sensitivity.
4. For every sample analyzed, verification is necessary to determine that method of standard addition is not required (see Exhibit E).
5. If method of standard addition is required, follow the procedure given in Exhibit E.

*This method may only be used under certain conditions (see D-83).

COPPER*

Method 220.2 CLP-M (Atomic Absorption, furnace technique)

Optimum Concentration Range: 5-100 ug/l

Approximate Detection Limit: 1 ug/l

Preparation of Standard Solution

1. Stock solution: Prepare as described under "direct aspiration method" (Exhibit D, Attachment 4).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".
3. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec-125°C.
2. Ashing Time and Temp: 30 sec-900°C.
3. Atomizing Time and Temp: 10 sec-2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 324.7 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 ul injection, continuous flow purge gas and non-pyrolytic graphite and are to be used as guidelines only. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. Background correction is required.
3. Nitrogen may also be used as the purge gas.
4. For every sample analyzed, verification is necessary to determine that method of standard addition is not required (see Exhibit E).
5. If method of standard addition is required, follow the procedure given in Exhibit E.

*This method may only be used under certain conditions (see D-83).

IRON*

Method 236.2 CLP-M (Atomic Absorption, furnace technique)

Optimum Concentration Range: 5-100 ug/l

Approximate Detection Limit: 1 ug/l

Preparation of Standard Solution

1. Stock solution: Prepare as described under "direct aspiration method" (Exhibit D, Attachment 4).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".
3. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec-125°C.
2. Ashing Time and Temp: 30 sec-1000°C.
3. Atomizing Time and Temp: 10 sec-2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 248.3 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 ul injection, continuous flow purge gas and non-pyrolytic graphite and are to be used as guidelines only. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is required.
3. Nitrogen may also be used as the purge gas.
4. For every sample analyzed, verification is necessary to determine that method of standard addition is not required (see Exhibit E).
5. If method of standard addition is required, follow the procedure given in Exhibit E.

*This method may only be used under certain conditions (see D-83).

MANGANESE*

Method 243.2 CLP-M (Atomic Absorption, furnace technique)

Optimum Concentration Range: 1-30 ug/l

Approximate Detection Limit: 0.2 ug/l

Preparation of Standard Solution

1. **Stock solution:** Prepare as described under "direct aspiration method" (Exhibit D, Attachment 4).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".
3. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrument Parameters (General)

1. **Drying Time and Temp:** 30 sec-125°C.
2. **Ashing Time and Temp:** 30 sec-1000°C.
3. **Atomizing Time and Temp:** 10 sec-2700°C.
4. **Purge Gas Atmosphere:** Argon
5. **Wavelength:** 279.5 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer MGA-2100, based on the use of a 20 ul injection, continuous flow purge gas and non-pyrolytic graphite and are to be used as guidelines only. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is required.
3. Nitrogen may also be used as the purge gas.
4. For every sample analyzed, verification is necessary to determine that method of standard addition is not required (see Exhibit E).
5. If method of standard addition is required, follow the procedure given in Exhibit E.

*This method may only be used under certain conditions (see D-83).

NICKEL*

Method 249.2 CLP-M (Atomic Absorption, furnace technique)

Optimum Concentration Range: 5-100 ug/l

Approximate Detection Limit: 1 ug/l

Preparation of Standard Solution

1. Stock solution: Prepare as described under "direct aspiration method" (Exhibit D, Attachment 4).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".
3. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec-125°C.
2. Ashing Time and Temp: 30 sec-900°C.
3. Atomizing Time and Temp: 10 sec-2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 232.0 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 ul injection, continuous flow purge gas and non-pyrolytic graphite and are to be used as guidelines only. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is required.
3. Nitrogen may also be used as the purge gas.
4. For every sample analyzed, verification is necessary to determine that method of standard addition is not required (see Exhibit E).
5. If method of standard addition is required, follow the procedure given in Exhibit E.

*This method may only be used under certain conditions (see D-83).

VANADIUM*

Method 286.2 CLP-M (Atomic Absorption, furnace technique)

Optimum Concentration Range: 10-200 ug/l

Approximate Detection Limit: 4 ug/l

Preparation of Standard Solution

1. Stock solution: Prepare as described under "direct aspiration method" (Exhibit D, Attachment 4).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions."
3. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec-125°C.
2. Ashing Time and Temp: 30 sec-1400°C.
3. Atomizing Time and Temp: 15 sec-2800°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 318.4 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer MGA-2100, based on the use of a 20 ul injection, continuous flow purge gas and pyrolytic graphite and are to be used as guideline only. Smaller size furnace devices or those employing faster rate of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is required.
3. Because of possible chemical interaction, nitrogen should not be used as the purge gas.
4. For every sample analyzed, verification is necessary to determine that method of standard addition is not required (see Exhibit E).
5. If method of standard addition is required, follow the procedure given in Exhibit E.

*This method may only be used under certain condition (see D-83).

ZINC*

Method 289.2 CLP-M (Atomic Absorption, furnace technique)

Optimum Concentration Range: 0.2-4 ug/l

Approximate Detection Limit: 0.05 ug/l

Preparation of Standard Solution

1. Stock solution: Prepare as described under "direct aspiration method" (Exhibit D, Attachment 4).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".
3. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec-125°C.
2. Ashing Time and Temp: 30 sec-400°C.
3. Atomizing Time and Temp: 10 sec-2500°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 213.9 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 ul injection, continuous flow purge gas and non-pyrolytic graphite and are to be used as guidelines only. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is required.
3. Nitrogen may also be used as the purge gas.
4. The analysis of zinc by the graphite furnace is extremely sensitive and very subject to contamination from the work area, reagents, and pipet tips. Since all these factors affect the precision and accuracy, zinc should be analyzed by the direct aspiration procedure whenever possible.
5. For every sample analyzed, verification is necessary to determine that method of standard addition is not required (see Exhibit E).
6. If method of standard addition is required, follow the procedure given in Exhibit E.

*This method may only be used under certain condition (see D-83).

ALUMINUM*

Method 202.1 CLP-M** (Atomic Absorption, direct aspiration)

Optimum Concentration Range: 5-50 mg/l using a wavelength of 309.3 nm

Sensitivity: 1 mg/l

Approximate Detection Limit: 0.1 mg/l

Preparation of Standard Solution

1. Stock Solution: Carefully weigh 1,000 g of aluminum metal analytical reagent grade). Add 15 ml of conc. HCl and 5 ml conc. HNO₃ to the metal, cover the beaker and warm gently. When solution is complete, transfer quantitatively to a liter volumetric flask and make up to volume with deionized distilled water. 1 ml = 1 mg Al (1000 mg/l).
2. Potassium Chloride Solution: Dissolve 95 g potassium chloride (KCl) in deionized distilled water and make up to 1 liter.
3. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation. To each 100 ml of standard and sample alike add 2.0 ml potassium chloride solution.

Instrument Parameters (General)

1. Aluminum hollow cathode lamp
2. Wavelength: 309.3 nm
3. Fuel: Acetylene
4. Oxidant: Nitrous oxide
5. Type of flame: Fuel rich

Interferences

1. Aluminum is partially ionized in the nitrous oxide-acetylene flame. This problem may be controlled by the addition of an alkali metal (potassium, 1000 ug/ml) to both sample and standard solutions.

Notes

1. The following may also be used:
308.2 nm Relative Sensitivity 1
396.2 nm Relative Sensitivity 2
394.4 nm Relative Sensitivity 2.5
2. For concentration of aluminum below 0.3 mg/l, the furnace procedure (Method 202.2 CLP-M) is recommended.

*This method may only be used under certain conditions (see D-83)

**CLP-M Modified for the Contract Laboratory Program

ANTIMONY*

Method 204.1 CLP-M (Atomic Absorption, direct aspiration)

Optimum Concentration Range: 1-40 mg/l using a wavelength of 217.6 nm

Sensitivity: 0.5 mg/l

Approximate Detection Limit: 0.2 mg/l

Preparation of Standard Solution

1. Stock Solution: Carefully weigh 2.7426 g of antimony potassium tartrate (analytical reagent grade) and dissolve in deionized distilled water. Dilute to 1 liter with deionized distilled water. 1 ml = 1 mg Sb (1000 mg/l).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrumental Parameters (General)

1. Antimony hollow cathode lamp
2. Wavelength: 217.6 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Fuel lean

Interferences

1. In the presence of lead (1000 mg/l), a special interference may occur at the 217.6 nm resonance line. In this case the 231.1 nm antimony line should be used.
2. Increasing acid concentrations decrease antimony absorption. To avoid this effect, the acid concentration in the samples and in the standards must be matched.

Notes

1. For concentrations of antimony below 0.35 mg/l, the furnace procedure (Method 204.2 CLP-M) is recommended.

*This method may only be used under certain conditions (see D-83).

BARIUM*

Method 208.1 CLP-M (Atomic Absorption, direct aspiration)

Optimum Concentration Range: 1-20 mg/l using a wavelength of 553.6 nm

Sensitivity: 0.4 mg/l

Approximate Detection Limit: 0.1 mg/l

Preparation of Standard Solution

1. Stock Solution: Dissolve 1.7787 g of barium chloride ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, analytical reagent grade) in deionized distilled water and dilute to liter. 1 ml = 1 mg Ba (1000 mg/l).
2. Potassium chloride solution: Dissolve 95 g potassium chloride, KCl, in deionized distilled water and make up to 1 liter.
3. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. To each 100 ml of standard and sample alike add 2.0 ml potassium chloride solution. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrumental Parameters (General)

1. Barium hollow cathode lamp
2. Wavelength: 553.6 nm
3. Fuel: Acetylene
4. Oxidant: Nitrous oxide
5. Type of flame: Fuel rich

Interferences

1. The use of a nitrous oxide-acetylene flame virtually eliminates chemical interference; however, barium is easily ionized in this flame and potassium must be added (1000 mg/l) to standards and samples alike to control this effect.
2. If the nitrous oxide flame is not available and acetylene-air is used, phosphate, silicon and aluminum will severely depress the barium absorbance. This may be overcome by the addition of 2000 mg/l lanthanum.

Notes

1. For concentrations of barium below 0.2 mg/l, the furnace procedure (Method 208.2 CLP-M) is recommended.

*This method may only be used under certain conditions (see D-83).

BERYLLIUM*

Method 210.1 CLP-M (Atomic Absorption, direct aspiration)

Optimum Concentration Range: 0.052 mg/l using a wavelength of 234.9 nm

Sensitivity: 0.025 mg/l

Approximate Detection Limit: 0.005 mg/l

Preparation of Standard Solution

1. Stock Solution: Dissolve 11.6586 g of beryllium sulfate, BeSO_4 , in deionized distilled water containing 2 ml conc. nitric acid and dilute to 1 liter. 1 ml = 1 mg Be (1000 mg/l).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrumental Parameters (General)

1. Beryllium hollow cathode lamp
2. Wavelength: 234.9 nm
3. Fuel: Acetylene
4. Oxidant: Nitrous oxide
5. Type of flame: Fuel rich

Interferences

1. Sodium and silicon at concentrations in excess of 1000 mg/l have been found to severely depress the beryllium absorbance.
2. Bicarbonate ion is reported to interfere; however, its effect is eliminated when samples are acidified to a pH of 1.5.
3. Aluminum at concentrations of 500 ug/l is reported to depress the sensitivity of beryllium [Spectrochim Acta 22, 1325 (1966)].

Notes

1. For concentrations of beryllium below 0.02 mg/l, the furnace procedure (Method 210.2 CLP-M) is recommended.

*This method may only be used under certain conditions (see D-83).

CADMIUM*

Method 213.1 CLP-M (Atomic Absorption, direct aspiration)

Optimum Concentration Range: 0.052 mg/l using a wavelength of 228.8 nm

Sensitivity: 0.025 mg/l

Approximate Detection Limit: 0.005 mg/l

Preparation of Standard Solution

1. Stock Solution: Carefully weigh 2.282 g of cadmium sulfate ($3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$, analytical reagent grade) and dissolve in deionized distilled water. Make up to 1 liter with deionized distilled water. 1 ml = 1 mg Cd (1000 mg/l).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrumental Parameters (General)

1. Cadmium hollow cathode lamp
2. Wavelength: 228.8 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Oxidizing

Notes

1. For levels of cadmium below 20 ug/l, the furnace technique, Method 213.2 CLP-M is recommended.

*This method may only be used under certain conditions (see D-83).

CHROMIUM*

Method 218.1 CLP-M (Atomic Absorption, direct aspiration)

Optimum Concentration Range: 0.5-10 mg/l using a wavelength of 357.9 nm

Sensitivity: 0.25 mg/l

Approximate Detection Limit: 0.05 mg/l

Preparation of Standard Solution

1. Stock Solution: Dissolve 1.923 g of chromium trioxide (CrO_3 , reagent grade) in deionized distilled water. When solution is complete, acidify with redistilled HNO_3 and dilute to 1 liter with deionized distilled water. 1 ml = 1 mg Cr (1000 mg/l).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrument Parameters (General)

1. Chromium hollow cathode lamp
2. Wavelength: 357.9 nm
3. Fuel: Acetylene
4. Oxidant: Nitrous oxide
5. Type of flame: Fuel rich

Notes

1. The following wavelengths may also be used:
359.3 nm Relative Sensitivity 1.4
425.4 nm Relative Sensitivity 2
427.5 nm Relative Sensitivity 3
428.9 nm Relative Sensitivity 4
2. The fuel rich air-acetylene flame provides greater sensitivity but is subject to chemical and matrix interference from iron, nickel, and other metals. If the analysis is performed in a lean flame the interference can be lessened but the sensitivity will also be reduced.
3. The suppression of both Cr (III) and Cr (VI) absorption by most interfering ions in fuel rich air-acetylene flames is reportedly controlled by the addition of 1% ammonium bifluoride in 0.2% sodium sulfate [Talanta 20, 631 (1973)]. A 1% oxine solution is also reported to be useful.
4. For levels of chromium between 50 and 200 ug/l where the air-acetylene flame cannot be used or for levels below 50 ug/l, the furnace procedure is recommended. See Method 218.2 CLP-M for the furnace procedure.

*This method may only be used under certain conditions (see D-83).

COBALT*

Method 219.1 CLP-M (Atomic Absorption, direct aspiration)

Optimum Concentration Range: 0.5-5 mg/l using a wavelength of 240.7 nm

Sensitivity: 0.2 mg/l

Approximate Detection Limit: 0.05 mg/l

Preparation of Standard Solution

1. Stock Solution: Dissolve 4.307 g of cobaltous chloride ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ analytical reagent grade), in deionized distilled water. Add 10 ml of concentrated nitric acid and dilute to 1 liter with deionized distilled water. 1 ml = 1 mg Co (1000 mg/l).
2. Prepare dilutions of the stock cobalt solution to be used as calibration standards at the time of analysis. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrument Parameters (General)

1. Cobalt hollow cathode lamp
2. Wavelength: 240.7 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Oxidizing

Notes

1. For levels of cobalt below 100 ug/l the furnace technique, Method 219.2 CLP-M is recommended.

*This method may only be used under certain conditions (see D-83).

COPPER*

Method 220.1 CLP-M (Atomic Absorption, direct aspiration)

Optimum Concentration Range: 0.2-5 mg/l using a wavelength of 324.7 nm

Sensitivity: 0.1 mg/l

Approximate Detection Limit: 0.02 mg/l

Preparation of Standard Solution

1. Stock Solution: Carefully weigh 100 g of electrolyte Copper (analytical reagent grade). Dissolve in 5 ml redistilled HNO_3 and make up to 1 liter with deionized distilled water. Final concentration is 1 mg Cu per ml (1000 mg/l).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrumental Parameters (General)

1. Copper hollow cathode lamp
2. Wavelength: 324.7 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Oxidizing

Notes

1. For levels of copper below 50 ug/l the furnace technique, Method 220.2 CLP-M is recommended.
2. Numerous absorption lines are available for the determination of copper. By selecting a suitable absorption wavelength, copper samples may be analyzed over a very wide range of concentration. The following lines may be used:

327.4 nm Relative Sensitivity 2
216.5 nm Relative Sensitivity 7
222.5 nm Relative Sensitivity 20

*This method may only be used under certain conditions (see D-83).

IRON*

Method 236.1 CLP-M (Atomic Absorption, direct aspiration)

Optimum Concentration Range: 0.3-5 mg/l using a wavelength of 248.3 nm

Sensitivity: 0.12 mg/l

Approximate Detection Limit: 0.03 mg/l

Preparation of Standard Solution

1. Stock Solution: Carefully weigh 1.000 g of pure iron wire (analytical reagent grade) and dissolve in 5 ml redistilled HNO_3 , warming if necessary. When solution is complete, make up to 1 liter with deionized distilled water. 1 ml = 1 mg Fe (1000 mg/l).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrumental Parameters (General)

1. Iron hollow cathode lamp
2. Wavelength: 248.3 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Oxidizing

Notes

1. The following wavelengths may also be used:
248.8 nm Relative Sensitivity 2
271.9 nm Relative Sensitivity 4
302.1 nm Relative Sensitivity 5
252.7 nm Relative Sensitivity 6
372.0 nm Relative Sensitivity 10
2. For concentrations of iron below 0.05 mg/l the furnace procedure, Method 236.2 CLP-M, is recommended.

*This method may only be used under certain conditions (see D-83).

LEAD*

Method 239.1 CLP-M (Atomic Absorption, direct aspiration)

Optimum Concentration Range: 1-20 mg/l using a wavelength of 283.3 nm

Sensitivity: 0.5 mg/l

Approximate Detection Limit: 0.1 mg/l

Preparation of Standard Solution

1. Stock Solution: Carefully weigh 1.599 g of lead nitrate, $\text{Pb}(\text{NO}_3)_2$ (analytical reagent grade), and dissolve deionized distilled water. When solution is complete acidify with 10 ml redistilled HNO_3 and dilute to 1 liter with deionized distilled water. 1 ml = 1 mg Pb (1000 mg/l).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrumental Parameters (General)

1. Lead hollow cathode lamp
2. Wavelength: 283.3 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Oxidizing

Notes

1. The analysis of this metal is exceptionally sensitive to turbulence and absorption bands in the flame. Therefore, some care should be taken to position the light beam in the most stable, center portion of the flame. To do this, first adjust the burner to maximize the absorbance reading with a lead standard. Then, aspirate a water blank and make minute adjustments in the burner alignment to minimize the signal.
2. The levels of lead below 200 ug/l the furnace technique, Method 239.2 CLP-M, is recommended.
3. The following wavelengths may also be used:
217.0 nm Relative Sensitivity 0.4
261.4 nm Relative Sensitivity 10

*This method may only be used under certain conditions (see D-83).

MANGANESE*

Method 243.1 CLP-M (Atomic Absorption, direct aspiration)

Optimum Concentration Range: 0.1-3 mg/l using a wavelength of 279.5 nm

Sensitivity: 0.05 mg/l

Approximate Detection Limit: 0.01 mg/l

Preparation of Standard Solution

1. **Stock Solution:** Carefully weigh 1.000 g of manganese metal (analytical reagent grade), and dissolve in 10 ml redistilled HNO_3 . When solution is complete, dilute to 1 liter with 1X (v/v) HCl.
1 ml = 1 mg Mn (1000 mg/l).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrumental Parameters (General)

1. Manganese hollow cathode lamp
2. Wavelength: 279.5 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Oxidizing

Notes

1. For levels of manganese below 25 ug/l, the furnace procedure, Method 243.2 CLP-M, is recommended.
2. The following line may also be used:
403.1 nm Relative Sensitivity 10.

*This method may only be used under certain conditions (see D-83).

NICKEL*

Method 249.1 CLP-M (Atomic Absorption, direct aspiration)

Optimum Concentration Range: 0.3-5 mg/l using a wavelength of 232.0 nm

Sensitivity: 0.15 mg/l

Approximate Detection Limit: 0.04 mg/l

Preparation of Standard Solution

1. Stock Solution: Dissolve 4.953 g of nickel nitrate, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (analytical reagent grade) in deionizing distilled water. Add 10 ml of conc. nitric acid and dilute to 1 liter deionized distilled water. 1 ml = 1 mg Ni (1000 mg/l).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrumental Parameters (General)

1. Nickel hollow cathode lamp
2. Wavelength: 232.0 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Oxidizing

Interferences

1. The 352.4 nm wavelength is less susceptible to spectral interference and may be used. The calibration curve is more linear at this wavelength; however, there is some loss of sensitivity.

Notes

1. For levels of nickel below 100 ug/l the furnace technique, Method 249.2 CLP-M, is recommended.

*This method may only be used under certain conditions (see D-83).

SILVER*

Method 272.1 CLP-M (Atomic Absorption, direct aspiration)

Optimum Concentration Range: 0.1-4 mg/l using a wavelength of 328.1 nm

Sensitivity: 0.06 mg/l

Approximate Detection Limit: 0.01 mg/l

Preparation of Standard Solution

1. Stock Solution: Dissolve 1.575 g of AgNO_3 , (analytical reagent grade) in deionized distilled water, add 10 ml conc. HNO_3 and make up to 1 liter. 1 ml = 1 mg Ag (1000 mg/l).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.
3. Iodine Solution, 1 N: Dissolve 20 grams of potassium iodide, KI (analytical reagent grade) in 50 ml of deionized distilled water, add 12.7 grams of iodine, I_2 , (analytical reagent grade) and dilute to 100 ml. Store in a brown bottle.
4. Cyanogen Iodide (CNI) Solution: To 50 ml of deionized distilled water add 4.0 ml conc. NH_4OH , 6.5 grams KCN, and 5.0 ml of 1.0 N I_2 solution. Mix and dilute to 100 ml with deionized distilled water. Fresh solution should be prepared every two weeks.⁽¹⁾

Instrumental Parameters (General)

1. Silver hollow cathode lamp
2. Wavelength: 328.1 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Oxidizing

Notes

1. For levels of silver below 30 ug/l the furnace procedure, Method 272.2 CLP-M, is recommended.
2. Silver nitrate standards are light sensitive. Dilutions of the stock should be discarded after use as concentrations below 10 mg/l are not stable over long periods of time.
3. If absorption to container walls or the formation of AgCl is suspected, make the sample basic using conc. NH_4OH and add 1 ml of (CNI) solution per 100 ml of sample. Mix the sample and allow to stand for 1 hour before proceeding with the analysis.⁽¹⁾

*This method may only be used under certain conditions (see D-83).

Method 272.1 CLP-M (cont.)

4. The 338.2 nm wavelength may also be used. This has a relative sensitivity of 2.

References

1. "The Use of Cyanogen Iodide (CNI) as a Stabilizing Agent for Silver in Photographic Processing Effluent Sample", Overbach, Daniel, Photographic Technology Division, Eastman Kodak Company, Rochester, N.Y. 14650.

THALLIUM*

Method 279.1 CLP-M (Atomic Absorption, direct aspiration)

Optimum Concentration Range: 1-20 mg/l using a wavelength of 276.8 nm
Sensitivity: 0.5 mg/l
Approximate Detection Limit: 0.1 mg/l

Preparation of Standard Solution

1. Stock Solution: Dissolve 1.303 g of thallium nitrate, $TlNO_3$ (analytical reagent grade) in deionized distilled water. Add 10 ml of conc. nitric acid and dilute to 1 liter with deionized distilled water. 1 ml = 1 mg Tl (1000 mg/l).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards must be prepared using nitric acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrumental Parameters (General)

1. Thallium hollow cathode lamp
2. Wavelength: 276.8 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Oxidizing

Notes

1. For concentrations of thallium below 0.2 mg/l, the furnace procedure, Method 279.2 CLP-M, is recommended.

*This method may only be used under certain conditions (see p-83).

VANADIUM*

Method 286.1 CLP-M (Atomic Absorption, direct aspiration)

Optimum Concentration Range: 2-100 mg/l using a wavelength of 318.4 nm

Sensitivity: 0.8 mg/l

Approximate Detection Limit: 0.2 mg/l

Preparation of Standard Solution

1. Stock Solution: Dissolve 1.7854 g of vanadium pentoxide, V_2O_5 (analytical reagent grade) in 10 ml of conc. nitric acid and dilute to 1 liter with deionized distilled water.
1 ml = 1 mg V (1000 mg/l).
2. Aluminum nitrate solution: Dissolve 139 g aluminum nitrate, $Al(NO_3)_3 \cdot 9H_2O$, in 150 ml of deionized distilled water; heat to effect solution. Allow to cool and make up to 200 ml.
3. Prepare dilutions of the stock vanadium solution to be used as calibration standards at the time of analysis. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation. To each 100 ml of standard and sample alike, add 2 ml of the aluminum nitrate solution.

Instrumental Parameters (General)

1. Vanadium hollow cathode lamp
2. Wavelength: 318.4 nm
3. Fuel: Acetylene
4. Oxidant: Nitrous Oxide
5. Type of flame: Fuel rich

Interferences

1. It has been reported that high concentrations of aluminum and titanium increase the sensitivity of vanadium. This interference can be controlled by adding excess aluminum (1000 ppm) to both samples and standards. [Talanta 15, 871 (1968)].

Notes

1. For concentrations of vanadium below 0.5 mg/l, the furnace procedure, Method 282.6 CLP-M, is recommended.

*This method may only be used under certain conditions (see D-83).

ZINC*

Method 289.1 CLP-M (Atomic Absorption, direct aspiration)

Optimum Concentration Range: 0.05-1 mg/l using a wavelength of 213.9 nm

Sensitivity: 0.02 mg/l

Approximate Detection Limit: 0.005 mg/l

Preparation of Standard Solution

1. Stock Solution: Carefully weigh 1.00 g of zinc metal (analytical reagent grade) and dissolve cautiously in 10 ml HNO_3 . When solution is complete make up to 1 liter with deionized distilled water. 1 ml = 1 mg Zn (1000 mg/l).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrumental Parameters (General)

1. Zinc hollow cathode lamp
2. Wavelength: 213.9 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Oxidizing

Notes

1. High levels of silicon may interfere.
2. The air-acetylene flame absorbs about 25% of the energy at the 213.9 nm line.
3. The sensitivity may be increased by the use of low-temperature flames.
4. Some container cap liners can be a source of zinc contamination. To circumvent or avoid this problem, the use of the polypropylene caps is recommended.
5. For concentration of zinc below 0.01 mg/l, the furnace procedure, Method 289.2 CLP-M, is recommended.

*This method may only be used under certain conditions (see D-83).

EXHIBIT E
QUALITY ASSURANCE/QUALITY CONTROL REQUIREMENTS

GENERAL QA/QC CONSIDERATIONS

Standard laboratory practices for laboratory cleanliness as applied to glassware and apparatus must be adhered to. Laboratory practices with regard to reagents, solvents, and gases should also be adhered to. For additional guidelines regarding these general laboratory procedures, please see Sections 4 and 5 of the Handbook for Analytical Quality Control in Water and Wastewater Laboratories EPA-600/4-79-019, USEPA Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, March 1979.

QUALITY ASSURANCE REQUIREMENTS

The quality assurance/quality control (QA/QC) procedures defined below must be used by the Contractor when performing the methods specified in Exhibit D. When additional QA/QC procedures are specified in the methods in Exhibit D, the Contractor must also follow these procedures. The cost of performing all QA/QC procedures specified in this Statement of Work is included in the price of performing the bid lot.

The purpose of this document is to provide a uniform set of procedures for the analysis of inorganic constituents of samples, documentation of methods and their performance during a survey, and verification of the sample data generated. The program will also assist laboratory personnel in recalling and defending their actions under cross examination if required to present court testimony in enforcement case litigation.

The prime function of the QA/QC program outlined here is the definition of procedures for the evaluation and documentation of sampling and analytical methodologies and the reduction and reporting of data. The objective is to provide a uniform basis for sample collection and handling, instrument and methods maintenance, performance evaluation, and analytical data gathering and reporting. Although it is impossible to address all analytical situations in one document, the approach taken here is to define minimum requirements for all major steps relevant to any inorganic analysis. In many instances where methodologies are available, specific quality control procedures are incorporated into the method documentation. Ideally, samples involved in enforcement actions are analyzed only after the methods have met the minimum performance and documentation requirements described in this document.

The Contractor must participate in the Laboratory Audit and Intercomparison Study Program run by EPA, EMSL-Las Vegas. The Contractor can expect to analyze two samples per three-month contract period for this program.

The Contractor must perform and report to SMO and EMSL/LV on Form XI quarterly verification of instrument detection limits (IDL) by the method specified in Exhibit E, by type and model for each instrument used on this contract. All the IDLs must meet the CRDLs specified in Exhibit C. For ICP methods, the Contractor must also report linearity range verification, all interelement correction factors, wavelengths used and integration times on a quarterly basis on Forms XII and XIII.

For QA/QC procedures, two different types of "samples" are specified. A "sample received" is the field or PE sample each of which has an EPA number. An "analytical sample" is each "analysis" performed (i.e. each cup, tube or container in autosamplers, etc). A "frequency of 10%" means once every 10 analytical samples. Calibration blanks and calibration verification samples are not counted as analytical samples when determining 10% frequency.

If any QC measurement fails to meet contract criteria the analytical measurement may be repeated only once prior to taking the appropriate corrective action as specified in Exhibit E.

The Contractor must report all QC data in the exact format shown in Forms II - XIII (See Exhibit B).

This section outlines the minimum QA/QC operations necessary to satisfy the analytical requirements of the contract. The following QA/QC operations must be performed as stated in this exhibit:

1. Initial Calibration and Calibration Verification
2. Continuing Calibration Verification
3. Preparation Blank Analysis
4. Interference Check Sample Analysis
5. ICP Serial Dilution Analysis
6. Matrix Spike Analysis
7. Duplicate Sample Analysis
8. Furnace AA QC Analysis (Method of Standard Additions may be required under certain conditions).
9. Laboratory Quality Control Sample Analysis
1. Initial Calibration and Calibration Verification

Guidelines for instrumental calibration are given in EPA 600/4-79-020 and/or Exhibit D. Instruments must be calibrated daily or once every 24 hours and each time the instrument is set up.

Instrument Calibration

For atomic absorption systems, calibration standards are prepared by diluting the stock metal solutions at the time of analysis. Low calibration standards must be prepared fresh each time an analysis is to be made and discarded after use. Prepare a blank and at least three calibration standards in graduated amounts in the appropriate range. One atomic absorption calibration standard must be at the CRDL except for mercury. The calibration standards must be prepared using the same type of acid or combination of acids and at the same concentration as will result in the samples following sample preparation. Beginning with the blank, aspirate or inject the standards and record the readings. If the AA instrument configuration prevents the required 4-point calibration, calibrate according to instrument manufacturer's recommendations, and analyze the remaining required standards. Results for these standards must be within

$\pm 5\%$ of the true value. Each standards concentration and the calculations to show that the $\pm 5\%$ criterion has been met, must be given in the raw data. If the values do not fall within this range, recalibration is necessary. The $\pm 5\%$ criteria does not apply to the atomic absorption calibration standard at the CRDL. Specific acceptance criteria will be set for this standard by EPA in the future. In the interim, the Contractor must observe and quantitate this standard at a level above their stated instrument detection limit during GFAA analysis. All standards must be reported on Form II, Part 2. Calibration standards for furnace procedures should be prepared as described in the individual methods for that metal.

Baseline correction is acceptable as long as it is performed after every sample or after the continuing calibration verification check. For cyanide and mercury, follow the calibration procedures outlined in Exhibit D. One cyanide calibration standard must be at the CRDL. For ICP systems, calibrate the instrument according to instrument manufacturer's recommended procedures.

Initial Calibration Verification Standards

Immediately after each of the ICP, AA and cyanide systems have been calibrated, the accuracy of the initial calibration shall be verified and documented for every analyte by the analysis of EPA Initial Calibration Verification Solution(s).

The initial calibration verification standard(s) must be run at each wavelength used for analysis.

If the Initial Calibration Verification Solution(s) are not available from EPA, or where a certified solution of an analyte is not available from any source, analyses shall be conducted on an independent standard at a concentration other than that used for calibration, but within the calibration range. An independent standard is defined as a standard composed of the analytes from a different source than those used in the standards for the initial calibration. For ICP, the Initial Calibration Verification Solution(s) must be run at each wavelength used in the analysis of the sample. When measurements exceed the control limits of Table 1, the analysis must be terminated, the problem corrected, the instrument recalibrated, and the calibration reverified. For CN, the initial calibration verification standard must be distilled.

The values for the initial and subsequent continuing calibration verifications shall be recorded on Form II (see Exhibit B) for ICP, AA, and cyanide analyses, as indicated.

Instrument Detection Limit Determination (IDL)

Before any field samples are analyzed under this contract, the instrumental detection limits (in ug/L) must be determined within 30 days of the start of the analyses and at least quarterly (every 3 months), and must meet the

levels specified in Exhibit C. The instrumental detection limits (in ug/L) shall be determined by multiplying by 3, the average of the standard deviations obtained on three nonconsecutive days from the analysis of a standard solution (each analyte in reagent water) at a concentration 3-5 times IDL, with 7 consecutive measurements per day. Each measurement must be performed as though it was a separate analytical sample (i.e., each measurement must be followed by a rinse and/or any other procedure normally performed between the analysis of separate samples). IDL's must be determined and reported for each wavelength used in the analysis of the samples.

For each Case, IDLs must be reported on QC Report Form VII. If multiple AA instruments are used for the analysis of an element within a Case, the highest IDL for the AAs must be reported for that Case. Use the same reporting procedure for multiple ICPs.

Linear Range Analysis (LRA)

To verify linearity near the CRDL for ICP analysis, the contractor must analyze an ICP standard at two times the CRDL or two times the IDL, whichever is greater, at the beginning and end of each sample analysis run, or a minimum of twice per 8 hour working shift, whichever is more frequent. This standard must be run for all elements analyzed by ICP except Al, Ba, Ca, Fe, Mg, Na and K. All standards must be reported on Form II, Part 2. Specific acceptance criteria for the standard will be set by EPA in the future. In the interim, the Contractor must observe and quantitate this standard at a level above the stated instrument-detection limit during ICP analysis.

For ICP analysis, a linear range verification check standard must be analyzed and reported quarterly for each element on Form XII. The standard must be analyzed during a routine analytical run performed under this contract. The analytically determined concentration of this standard must be within $\pm 5\%$ of the true value. This concentration is the upper limit of the ICP linear range beyond which results cannot be reported under this contract without dilution of the analytical sample.

Calibration Blank

A calibration blank is analyzed after initial calibration verification and each time the instrument is calibrated, and at a frequency of 10% or every 2 hours during the run, whichever is more frequent. The blank must be analyzed at the beginning of the run and after the last analytical sample. The results for the calibration blank solution shall be recorded on Form III for ICP, AA and cyanide analyses, as indicated. If the magnitude (absolute value) of the CB result exceeds the IDL (positive or negative) the result should be so reported in ug/L on Form III, otherwise report as IDL-U. If this blank result exceeds the window of \pm CRDL (Exhibit C), terminate analysis, correct the problem and recalibrate.

2. Continuing Calibration Verification

To assure calibration accuracy during each analysis run, one of the following standards is to be used for continuing calibration verification and must be analyzed for each analyte at a frequency of 10% or every 2 hours during an analysis run, whichever is more frequent. The standard must also be analyzed for each analyte at the beginning of the run and after the last analytical sample. The analyte concentrations in the continuing calibration standard must be one of the following solutions at or near the mid-range levels of the calibration curve:

1. EPA Solutions
2. NBS SRM 1643a
3. A contractor-prepared standard solution

TABLE 1. INITIAL AND CONTINUING CALIBRATION VERIFICATION
CONTROL LIMITS FOR INORGANIC ANALYSES

Analytical Method	Inorganic Species	% of True Value (EPA Set)	
		Low Limit	High Limit
ICP/AA	Metals	90	110
Cold Vapor AA	Mercury	80	120
Other	Cyanide	85	115

The same continuing calibration standard must be used throughout the analysis runs for a case of samples received.

If the deviation of the continuing calibration verification is greater than the Control Limits specified in Table 1, the instrument must be recalibrated and the preceding 10 samples reanalyzed for the analytes affected. Information regarding the continuing verification of calibration shall be recorded on Form II (see Exhibit B) for ICP, AA and cyanide as indicated.

3. Preparation Blank Analysis

At least one preparation blank (or reagent blank), consisting of deionized distilled water processed through each sample preparation procedure (i.e., water, solids) performed for each Case, must be prepared and analyzed with every 20 samples received, or with each batch* of samples digested whichever

*A group of samples prepared at the same time.

is more frequent (see Exhibit D). The first 20 samples of a Case are to be assigned to preparation blank one, and the second 20 samples to preparation blank two, etc. (see Form III). Each data package must contain the results of all the preparation blank analyses associated with the samples in that Case.

This blank is to be reported for each Case and used in all analyses to ascertain whether sample concentrations reflect contamination in the following manner:

1. If the concentration of the blank is less than or equal to the contract required detection level (Exhibit C), no correction of sample results is performed.
2. If the concentration of the blank is above the contract required detection level: For any group of samples associated with a particular blank, the concentration of the sample with the least concentrated analyte must be 10X the blank concentration, or all samples associated with the blank and less than 10X the blank concentration must be redigested and reanalyzed, with the exception of an identified aqueous-soil field blank. The sample value is not to be corrected for the blank value.

The values for the preparation blank shall be recorded in ug/L for aqueous samples and in mg/kg for solid samples on Form III (see Exhibit B) for ICP, AA, and cyanide analyses, as indicated.

4. ICP Interference Check Sample Analysis

To verify inter-element and background correction factors the Contractor must analyze and report the results for the ICP Interference Check Samples at the beginning and end of each analysis run (or a minimum of twice per 8 hour working shift, whichever is most frequent), but not before initial calibration verification. The ICP Interference Check Samples must be obtained from EPA (EML/LV) if available and analyzed according to the instructions supplied with the ICS. Results for the check sample analyses during the analytical runs must fall within the control limit of $\pm 20\%$ of the true value for the analytes included in the Interference Check Samples. For elements contained in the ICS, if true values are not supplied with the ICS, the mean must be determined by initially analyzing the ICS at least five times repetitively for the particular analytes. This mean determination must be made during an analytical run where the results for the previously supplied EPA ICS met all contract specifications. Additionally, the result of this initial mean determination is to be used as the true value for the lifetime of that solution (i.e., until the solution is exhausted). If the results are not within the control limits, terminate the analysis, correct the problem, recalibrate, reverify the calibration, and reanalyze the samples. If the ICP Interference Check Sample is not available from EPA, an independent ICP Check Sample must be prepared with interferent and analyte concentrations at the levels specified in Table 2 (Exhibit E). The mean value and standard deviation must be established by initially

analyzing the check samples at least 5 times repetitively for each parameter on Form IV. Results must fall within the control limit of $\pm 20\%$ of the established mean value, unless the out-of-control result is for an element not being reported from the ICP run. Results from the Interference Check Sample analyses must be recorded on Form IV for all ICP parameters (see Exhibit B).

5. ICP Serial Dilution Analysis

Prior to reporting concentration data for the analyte elements, the Contractor must analyze and report the results of the ICP Serial Dilution Analysis. The ICP Serial Dilution Analysis must be performed on each group of samples of a similar matrix type (i.e., water, soil) and concentration (i.e., low, medium) for each Case of samples, or for each 20 samples received, whichever is more frequent. Samples identified as field blanks cannot be used for serial dilution analysis. If the analyte concentration is sufficiently high (minimally a factor of 10 above the instrumental detection limit after dilution), an analysis of a 5 fold dilution must agree within 10% of the original determination. If the dilution analysis for one or more analytes is not within 10%, a chemical or physical interference effect should be suspected, and the data for all affected analytes in the samples received associated with that serial dilution must be flagged with an "E". In the instance where there is more than one serial dilution per case, if one serial dilution result is not within contract criteria, flag all the samples of the same matrix and concentration in the case. Serial dilution results and "E" flags must be reported on QC Report Form IX and I.

6. Spiked Sample Analysis

The spiked sample analysis is designed to provide information about the effect of the sample matrix on the digestion and measurement methodology. The spike is added before the digestion (i.e., prior to the addition of other reagents) and prior to any distillation steps (i.e., CN-). At least one spiked sample analysis must be performed on each group of samples of a similar matrix type (i.e., water, soil) and concentration (i.e., low, medium) for each Case of samples or for each 20 samples received, whichever is more frequent.* If the spike analysis is performed on the same sample that is chosen for the duplicate sample analysis, spike calculations must be performed using the results of the sample designated as the "original sample" (see Duplicate Sample Analysis). Do not use the average of the duplicate results for the purpose of determining percent recovery. Samples identified as field blanks cannot be used for spiked sample analysis. EPA may require that a specific sample be used for the spiked sample analysis. The analyte spike must be added in the amount given in Table 3 (Exhibit E) for each element analyzed. If two analytical methods are used to obtain the reported values for the same element for a Case of samples (i.e., ICP, GFAA), spike samples must be run by each method used. If the spike recovery is not within the limits of 75-125%, the data of all samples received associated with that spiked sample and determined by the same analytical method must be flagged with the letter "N" on Forms I and V. An exception to this rule is granted in situations where the sample concentration exceeds the spike concentration by a

factor of four or more. In such a case, the data shall be reported unflagged even if the percent recovery does not meet the 75-125% recovery criteria. For flame AA, ICP and Hg analyses, when the pre-digest spike recovery falls outside the control limits, and the sample result does not exceed 4x the spike added, a post-digest spike must be performed for those elements that do not meet the specified criteria (exception: Ag). Spike the unspiked aliquot of the sample at two times the indigenous level or two times the CRDL, whichever is greater. Results of the post-digest spike must be reported on QC Form V A. In the instance where there is more than one spiked sample per matrix and concentration per Case, if one spike sample recovery is not within contract criteria, flag all the samples of the same matrix in the Case. Individual component percent recoveries (XR) are calculated as follows:

$$XR_{\text{recovery}} = \frac{(SSR - SR)}{SA} \times 100$$

Where SSR = Spiked Sample Result
 SR = Sample Result
 SA = Spike Added

When sample concentration is less than the instrument detection limit, use SR = 0 only for purposes of calculating XR recovery. The spiked sample results, sample results and XR recovery (positive or negative) must be reported on Form V for ICP, AA and cyanide analyses, as indicated.

TABLE 2. INTERFERENT AND ANALYTE ELEMENTAL CONCENTRATIONS USED FOR ICP INTERFERENCE CHECK SAMPLE

Analytes	(mg/L)	Interferents	(mg/L)
Ba	0.5	Al	500
Be	0.5	Ca	500
Cd	1.0	Fe	200
Co	0.5	Hg	500
Cr	0.5		
Cu	0.5		
Mn	0.5		
Ni	1.0		
Pb	1.0		
V	0.5		
Zn	1.0		

TABLE 3. SPIKING LEVELS FOR SPIKED SAMPLE ANALYSIS

Element	For ICP/AA (ug/L)		For Furnace AA (ug/L)		Other (ug/L)
	Water	Sediment	Water	Sediment	
Aluminum	2,000	*			
Antimony	500	500	100	100	
Arsenic	2,000	2,000	40	40	
Barium	2,000	2,000			
Beryllium	50	50			
Cadmium	50	50	5	5	
Calcium	*	*			
Chromium	200	200			
Cobalt	500	500			
Copper	250	250			
Iron	1,000	*			
Lead	500	500	20	20	
Magnesium	*	*			
Manganese	500	500			
Mercury					1
Nickel	500	500			
Potassium	*	*			
Selenium	2,000	2,000	10	10	
Silver	50	50			
Sodium	*	*			
Thallium	2,000	2,000	50	50	
Vanadium	500	500			
Zinc	500	500			
Cyanide					100

NOTE: Elements without spike levels and not designated with an asterisk, should be spiked at appropriate levels.

The levels shown indicate concentrations in the final digestate of the spiked sample (200 mL FV)

*No spike required.

7. Duplicate Sample Analysis (DUP)

One duplicate sample must be analyzed from each group of samples of a similar matrix type (i.e., water, soil) and concentration (i.e., low, medium) for each Case of samples or for each 20 samples received, whichever is more frequent.* Results of the analyses for the original sample and the duplicate sample must be reported on separate Form I's as Form IA and Form IB. Do not average duplicates for reporting on Form I. Duplicate sample analyses are required for percent solids. Samples identified as field blanks cannot be used for duplicate sample analysis. EPA may require that a specific sample be used for duplicate sample analysis. If two analytical methods are used to obtain the reported values for the same element for a Case of samples (i.e., ICP, GFAA), duplicate samples must be run by each method used. The relative percent differences (RPD) for each component are calculated as follows:

$$RPD = \frac{|D1 - D2|}{(D1+D2)/2} \times 100$$

Where RPD = Relative Percent Difference
D1 = First Sample Value (original)
D2 = Second Sample Value (duplicate)

The results of the duplicate sample analysis must be reported on Form VI in ug/L for aqueous samples and mg/kg for solid samples. (See Exhibit B). A control limit of $\pm 20\%$ for RPD shall be used for sample values greater than or equal to 5 times the contract required detection level (CRDL). A control limit of \pm the CRDL shall be used for sample values less than 5 times the CRDL (Exhibit C), and this control limit (\pm CRDL) should be entered in the "Control Limit" column on Form VI. If one result is above the $5 \times$ CRDL level and the other is below, use the \pm CRDL criteria. If either sample value is less than the CRDL, the RPD is not calculated and is indicated as "NC" on Form VI. For solid duplicate results $< 5 \times$ CRDL, enter the value of \pm CRDL, corrected for sample weight and percent moisture, in the control limit column.

If the duplicate sample results are outside the control limits, flag all the data for samples received associated with that duplicate sample with an "*" on Forms I and VI. In the instance where there is more than one duplicate sample per Case, if one duplicate result is not within contract criteria, flag all the samples of the same matrix and concentration in the Case. The percent difference data will be used by EPA to evaluate the long-term precision of the methods for each parameter. Specific control limits for each element will be added to Form VI at a later date based on these precision results.

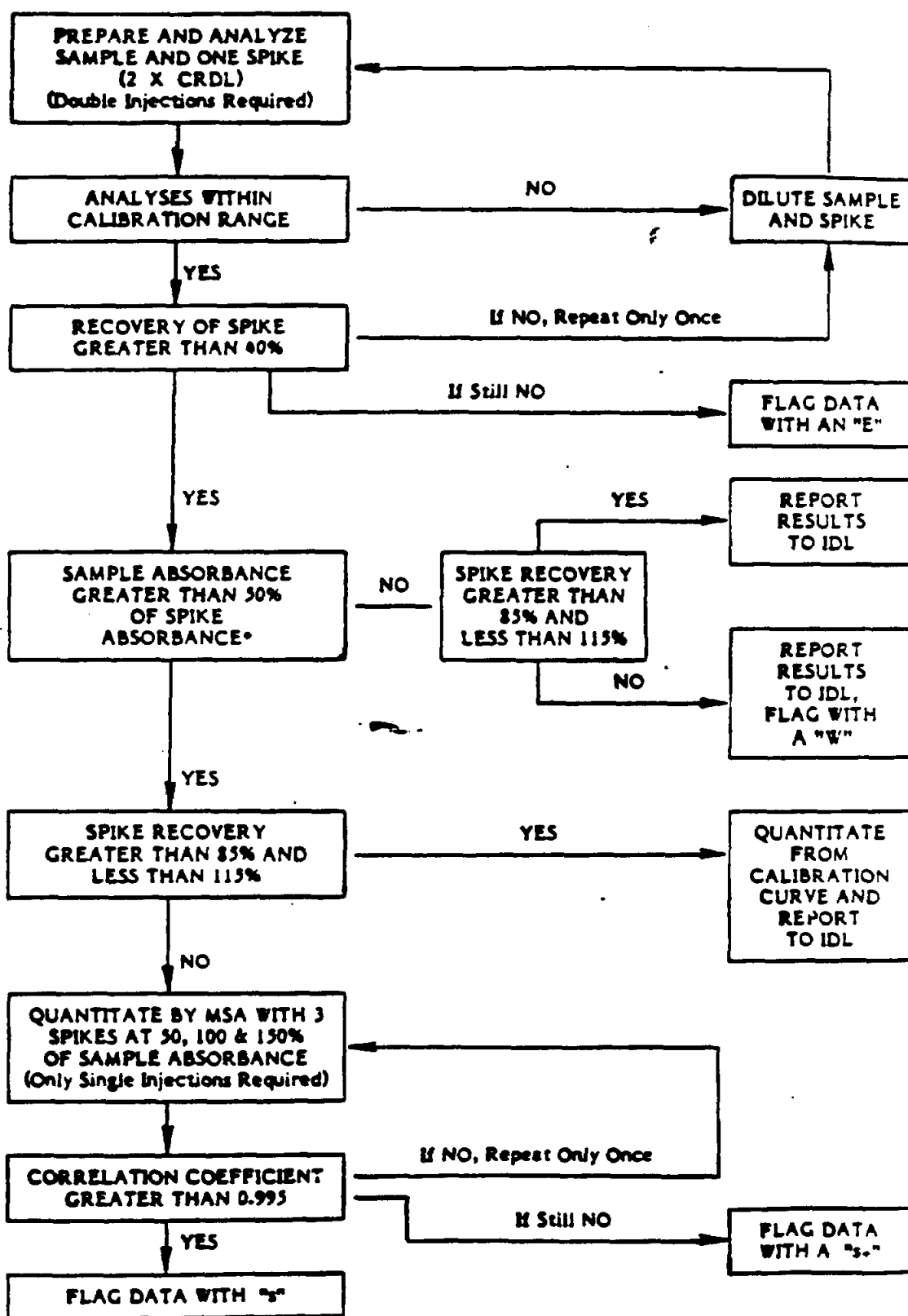
*EPA may require additional duplicates be analyzed, on request, for which the contractor will be paid.

+Relative percent difference is equivalent to relative range of duplicates (RR).

8. Furnace Atomic Absorption (AA) QC Analysis

Because of the nature of the Furnace AA technique, the special procedures summarized in Figure 1 will be required for quantitation. (These procedures are not meant to replace those included in Exhibit D of this document, but will supplement the guidance provided therein.)

Figure 1.
FURNACE ATOMIC ABSORPTION ANALYSIS SCHEME



*Spike absorbance defined as (absorbance of spike sample) minus (absorbance of the sample).

1. All furnace analyses, except during Full Methods of Standard Addition (MSA), will require duplicate injections for which the average absorbance or "concentration" will be reported. All analyses must fall within the calibration range. The raw data package must contain absorbance or "concentration" values for both injections, the average value and the relative standard deviation (RSD) or coefficient of variation (CV). For concentrations greater than CRDL, the duplicate injection readings must agree within 20% RSD or CV, or the sample must be rerun once (i.e., two additional burns). If the readings are still out, flag the value with an "M" on Form I.
2. All furnace analyses for each sample, including the LCS, will require at least a single analytical spike to determine if the MSA will be required for quantitation. An analytical spike is not required on the predigest spike sample when the predigest spike sample recovery is within the specified control limits of 75 - 125 % or when the sample concentration is greater than 4x the predigest spike concentration. The spike* will be required to be at a concentration (in the sample) twice the contract required detection limit (CRDL). The percent (XR) of the spike, calculated by the same formula as Spiked Sample analyses (Exhibit E), will then determine how the sample will be quantitated as follows:
 - a) If the spike recovery is less than 40%, the sample must be diluted and rerun with another spike. Dilute the sample by a factor of 5 to 10 and rerun. This step must only be performed once. If after the dilution the spike recovery is still <40%, report data and flag with an "E" to indicate interference problems.
 - b) If the spike recovery is greater than 40% and the sample absorbance or concentration is <50% of the spike+, report the sample results to the IDL. If the spike recovery is less than 85% or greater than 115%, flag the result with an "W".
 - c) If the sample absorbance or concentration is >50% of the spike+ and the spike recovery is between 85% and 115%, the sample should be quantitated directly from the calibration curve and report to the IDL.
 - d) If the sample absorbance or concentration is >50% of the spike+ and the spike recovery is less than 85% or greater than 115%, the sample must be quantitated by MSA.
3. The following procedures will be incorporated into MSA analyses.
 - a) Data from MSA calculations must be within the linear range as determined by the calibration curve generated at the beginning of the analytical run.

*Spikes are post digest spikes to be prepared prior to analysis by adding a known quantity of the analyte to an aliquot of the digested sample. The unspiked sample aliquot must be compensated for any volume change in the spike samples by addition of deionized water to the unspiked sample aliquot.

+ "Spike" is defined as (absorbance or concentration of spike sample) minus (absorbance or concentration of the sample).

- b) The sample and three spikes must be analyzed consecutively for MSA quantitation (the "initial" spike run data is specifically excluded from use in the MSA quantitation). Only single injections are required for MSA quantitation. Each full MSA counts as 2 "analytical samples" towards determining 10% QC frequency (i.e., 5 full MSAs can be performed between calibration verifications).
- c) For analytical runs containing only MSAs, single injections can be used for QC samples during that run.
- d) Spikes* should be prepared such that:
 - Spike 1 is approximately 50% of the sample absorbance.
 - Spike 2 is approximately 100% of the sample absorbance.
 - Spike 3 is approximately 150% of the sample absorbance.
- e) The data for each MSA analysis should be clearly identified in the raw data documentation along with the slope, intercept and correlation coefficient (r) for the least squares fit of the data and the results reported on Form VIII. Reported values obtained by MSA are flagged on the data sheet (Form I) with the letter "s".
- f) If the correlation coefficient (r) for a particular analysis is less than 0.995 the MSA analyses must be repeated once. If the correlation coefficient is still <0.995, report the results on Form I from the run with the best "r" and flag the result with a "t".

9. Laboratory Control Sample Analysis

Laboratory Control Samples (LCS) - Aqueous and solid laboratory quality control samples must be analyzed for each analyte using the same sample preparations, analytical methods and QA/QC procedures employed for the EPA samples received.

The aqueous LCS solution must be obtained from EPA (if unavailable, the EPA Initial Calibration Verification solutions may be used). The aqueous LCS must be prepared and analyzed with the aqueous samples for each of the procedures applied to each case of samples received. One aqueous LCS must be analyzed for every 20 aqueous samples received, or for each batch* of aqueous samples digested whichever is more frequent (see Exhibit D). For cyanide, the distilled mid-range calibration standard may be used as the aqueous LCS (see Section 8.3.2.1, Exhibit D). An aqueous LCS is not required for mercury analysis.

*A group of samples prepared at the same time.

The solid LCS, available from EMSL/LV, must be prepared and analyzed using each of the procedures applied to the solid samples received (exception: percent solids determination not required). If this EPA solid LCS is unavailable, other EPA Quality Assurance Check samples or other certified materials may be used. One solid LCS must be analyzed for every 20 solid samples received, or for each batch of samples digested, whichever is more frequent (see Exhibit D).

All LCS results will be reported on Form VII in terms of true concentration and percent recovery (XR) as calculated by:

$$XR = (\text{Observed/True}) \times 100$$

where "observed" is the measured concentration.

If the % recovery for the aqueous LCS falls outside the control limits of 80 - 120% (exception: Ag and Sb), the analyses must be terminated, the problems corrected and the previous samples associated with that LCS redigested and reanalyzed (i.e., previous 19 samples or the batch of samples from the case).

If the results for the solid LCS fall outside the control limits established by EPA, the analyses must be terminated, the problem corrected and the previous samples associated with that LCS redigested and reanalyzed (i.e., previous 19 samples or the batch of samples from the case).

II. LABORATORY AUDIT PROCEDURE

This section outlines the procedures which will be used by the Project Officer or authorized representative in order to allow the continued analysis of water and soil/sediment samples for the inorganic parameters contained in the contract. Laboratory performance is measured by four major procedures: 1) Analysis of performance evaluation (PE) samples, 2) Inorganic Data Audits conducted at EMSL-LV, 3) Trend analysis of laboratory quality control data, and 4) On-site inspection of the laboratory to verify continuity of personnel, instrumentation and quality control functions. The following is a description of these four procedures.

Part 1 Performance Evaluation Sample Analysis

The Performance Evaluation (PE) sample set will be sent to a participating laboratory on a quarterly basis to verify the laboratory's continuing ability to produce acceptable analytical results. These samples will be provided either single blind (recognizable as a PE material and of unknown composition), or double blind (not recognizable as a PE material and of unknown composition). Contractors are required to return PE analytical data within the specifications of the contract reporting schedule (Exhibit B). The PE sample will contain a representative array of inorganic compounds that would normally be the subject of analysis under this contract. Levels in the PE sample will be consistent with those expected in routine environmental samples.

When the PE data are received, results will be scored routinely for identification and quantitation, according to the elements and weighting factors shown in Figure 1. Results of this scoring will be provided for the contractor via coded evaluation spread sheets by compound analysis. The government reserves the right to adjust the scores on any given PE sample, due to unanticipated difficulties with a particular sample. If a laboratory is remiss in its ability to perform acceptably, they will be so notified immediately. A laboratory so notified may expect, but the government is not limited to, a site visit and a full data audit, so that corrective action may be taken immediately. Corrective action for an inorganic contract may include analysis of a second PE sample which the government may provide. Failure to take corrective action and/or failure of two successive inorganic PE samples may require that the laboratory must stop analysis of routine environmental samples, until such time as the Contract Officer has determined that they may resume analysis.

The government reserves the right to revise the scoring procedure.

Laboratory _____ Date _____

Quarter (circle one): 1 2 3 4 FY _____

I. Sample I, Case _____ Points Awarded _____

A. Identification (maximum of 10 points possible)
(number of parameters present reported below
detection limit (____) x 10/number of parameters
present (____) = _____ deducted)

B. Quantitation (maximum of 35 points possible)
(number of parameters not within acceptance
criteria (____) x 35/number of parameters in
sample (____) = _____ deducted)

C. False positives (maximum of 5 points possible)
(number of non-present parameters reported as
>CRDL (____) x 5/number of non-present param-
eters in the sample (____) = _____ deducted)

Sample I Raw Point Score = _____

Sample I Raw Percent Score = _____

Timeliness (minus 1% per day from the Raw Score
for this sample for each day this sample's data
package is delivered after the 31st day following
the documented day of sample receipt =
_____ % deducted)

Sample I Net Percent Score = _____

II. Sample II, Case _____

A. Identification (maximum of 10 points possible)
(number of parameters present reported below
detection limit (____) x 10/number of parameters
present (____) = _____ deducted)

(continued)

Figure 1. Inorganic PE sample score sheet.

Figure 1. (Continued)

II. Sample II, Case _____ (Continued)	Points Awarded
B. Quantitation (maximum of 35 points possible) (number of parameters not within acceptance criteria (____) x 35/number of parameters in the sample (____) = ____ deducted)	_____ _____
C. False positives (maximum of 5 points possible) (number of non-present parameters reported as >CRDL (____) x 5/number of non-present param- eters in the sample (____) = ____ deducted)	_____ _____
Sample II Raw Point Score =	_____
Sample II Raw Percent Score =	_____
Timeliness (minus 1% per day from the Raw Score for this sample for each day this sample's data package is delivered after the 31st day following the documented day of sample receipt = ____% deducted)	_____ _____
Sample II Net Percent Score =	_____

III. Summary of Scoring

Maximum Score for Samples I and II _____ points

Raw Score for Samples I and II _____ points

Raw Percent Score for Samples I and II _____ percent

Net Percent Score for Samples I and II _____ percent

Part 2 Inorganic Data Audits

Data audits on the data packages received at EMSL-LV are conducted to ensure an acceptable level of laboratory quality, identify laboratories consistently below a minimum quality level, and identify contractual problems in the CLP. Cases will be reviewed for analytical reporting, documentation, and other types of errors. A numerical evaluation of data quality will be assigned to cases using an audit mechanism such as Military Standard 105D.

Cases are selected for audit on a random basis. Three inspection levels are possible: normal, reduced, or tightened. Tightened inspection will be initiated upon rejection of any case. Normal inspection levels will be resumed when the laboratory consistently submits acceptable data. Reduced inspection levels will be adopted after a laboratory has consistently submitted acceptable data over a long period.

The data audit procedure classifies errors into three categories depending on the seriousness of the error. Critical errors affect the validity of the entire case, major errors affect the validity of the individual analyses, and minor errors affect the technical content of a case, but are easily resolved.

Mil Std (Military Standard) 105D may be used to determine a specific acceptable quality level (AQL) based on submitted data from all contract laboratories. The Agency can then identify individual laboratories consistently below the AQL, identify specific problems, and address the problems in a timely fashion through an increase in the data audit procedure, or through additional on-site evaluations, or a combination of both.

The government reserves the right to revise these audit procedures as required.

Part 3 Trend Analysis

Monitoring of quality control data produced during contract laboratory analysis is performed by entry into a computer data base called the Automated Data Review Organic Inorganic TCDD (ADROIT). Data entry is accomplished from the contract specified forms. Deviation from the contractually specified forms is unacceptable. Production of these data base reports has been continuous since November 1982 and has been the basis of protocol revision for all three areas of analysis. The reports now provide the capability of trend analysis in the quality control data produced from the laboratories. These reports are capable of producing laboratory, case, and sample number specific data anomalies or trends for the following areas:

- | | |
|----------------------|------------------------------|
| * Preparation Blanks | * Laboratory Control Samples |
| * Matrix Spikes | * Calibration Verifications |
| * Duplicates | * Under development |

Program-wide statistical results are used to rank laboratories in order to determine the relative performance of each laboratory in a given protocol (between laboratory trends). These reports are also used to evaluate trends within laboratories. The results of the trend analyses are included in overall evaluation of laboratory performance.

Laboratory performances will be monitored over time using these trend analysis techniques to detect departures of laboratory output from required levels of performance.

Part 4. On-site Laboratory Evaluation:

The on-site laboratory evaluations help to assure that all the necessary quality control is being applied by the laboratory in order to deliver a quality product. Quality assurance evaluations allow the evaluators to determine that:

- 1) The Organization and Personnel are qualified to perform assigned tasks,
- 2) Adequate Facilities and Equipment are available,
- 3) Complete Documentation, including chain-of-custody of samples is being implemented,
- 4) Proper Analytical Methodology is being used,
- 5) Adequate analytical Quality Control, including reference samples, control charts, and documented corrective action measures, is being provided, and
- 6) Acceptable Data Handling and documentation techniques are being used.

The on-site visit also serves as a mechanism for discussing weaknesses identified through the Performance Evaluation sample analysis. Lastly, the on-site visit allows the evaluation team to determine if the laboratory has implemented the recommended and/or required corrective actions, with respect to quality assurance, made during the previous on-site visit.

The following describes the protocol which is followed during a laboratory evaluation. Included is an Inorganic Laboratory Evaluation Checksheet (ILEC). A similar ILEC will be used in future on-site laboratory evaluations in order to maintain a continuous record. The government reserves the right to change the ILEC as changing conditions dictate.

I. Event Sequence for the Laboratory Evaluation

A. Meeting with Laboratory Manager and Project Manager

1. Introduction
2. Discuss purpose of visit
3. Review of personnel changes

B. Review of Previous Trip Report

The most recent report is reviewed to verify that all previously identified problems have been corrected.

C. Laboratory Tour

At this stage of the evaluation process, a laboratory tour is performed. The tour follows the path of a sample starting from sample receipt to final compilation, review, and distribution of the data generated by sample analysis. Photographs may be taken during the tour.

D. Review of Data Audit Report(s)

Questions or problems noted in the data audit report, performance evaluation studies, or comments from users of the data are discussed at this stage of the evaluation process. The review of data generated by the laboratory may necessitate complete examination of all documentation associated with the sample(s) in question.

E. Documentation Procedures

An evidentiary audit of chain-of-custody and similar procedures is conducted by the Contract Evidence Audit Team (CEAT), which is under contract to the USEPA National Enforcement Investigation Center, Denver, Colorado.

F. Debriefing

All weaknesses identified during the laboratory evaluation are discussed. Weaknesses which have not been corrected may be cause for penalties or contract termination.

Inorganic Laboratory Evaluation Checksheet (ILEC)

Laboratory: _____

Date: _____

Type of Evaluation: _____

Contract Number: _____

Contract Title: _____

Personnel Contacted: _____

Name	Title
_____	_____
_____	_____
_____	_____
_____	_____
_____	_____
_____	_____
_____	_____

Laboratory Evaluation Team:

Name	Title
_____	_____
_____	_____
_____	_____
_____	_____
_____	_____
_____	_____
_____	_____

Low/Medium Inorganic Laboratory Evaluation Checklist

I ORGANIZATION AND PERSONNEL (page 1 of 2)

ITEM	YES	NO	COMMENT
Laboratory or Project Manager (individual responsible for overall technical effort): Name: _____			
Inductively Coupled Plasma Emission Spectroscopist Name: _____ Experience: 1 year minimum requirement			
Flameless Atomic Absorption Spectroscopist Name: _____ Experience: 1 year minimum requirement			
Inorganic Sample Preparation Expert Name: _____ Experience: 3 months minimum requirement			
Flame and Cold Vapor AA Spectroscopist Name: _____ Experience: 9 months minimum requirement			
Classical Inorganic Techniques Analyst: Name: _____ Experience: 6 months minimum requirement			
Do personnel assigned to this project have the appropriate <u>educational background</u> to successfully accomplish the objectives of the program?			

I ORGANIZATION AND PERSONNEL (Page 2 of 2)

ITEM	YES	NO	COMMENT
Do personnel assigned to this project have the appropriate level and type of experience to successfully accomplish the objectives of this program?			
Is the organization adequately staffed to meet project commitments in a timely manner?			
Does the laboratory Quality Assurance Supervisor report to senior management levels?			
Was the Project Manager available during the evaluation?			
Was the Quality Assurance Supervisor available during the evaluation? Name: _____			

Additional Comments

II. Sample Receipt and Storage Area

ITEM	YES	NO	COMMENT
Is a sample custodian designated? If yes, name of sample custodian. Name: _____			
Are written Standard Operating Procedures (SOP) developed for receipt and storage of samples?			
Is the appropriate portion of the SOP available to the analyst at the sample receipt/storage area?			
Are the sample shipping containers opened in a manner which prevents possible laboratory contamination?			
Are samples that require preservation stored in such a way as to maintain their preservation?			
Are adequate facilities provided for storage of samples, including cold storage?			
Is the temperature of the cold storage recorded daily in a logbook?			
Are the sample receipt/storage and temperature logbooks maintained in a manner consistent with GLP?			
Has the supervisor of the individual maintaining the notebook personally examined and reviewed the notebook periodically, and signed his/her name therein, together with the date and appropriate comments as to whether or not the notebook is being maintained in an appropriate manner.			

Additional Comments

[illegible]

III. Sample Preparation Area

When touring the facilities, give special attention to: (a) the overall appearance of organization and neatness, (b) the proper maintenance of facilities and instrumentation, (c) the general adequacy of the facilities to accomplish the required work.

ITEM	YES	NO	COMMENT
Is the laboratory maintained in a clean and organized manner?			
Does the laboratory appear to have adequate workspace (120 sq. feet, 6 linear feet of unencumbered bench space per analyst)?			
Are the toxic chemical handling areas either a stainless steel bench or an impervious material covered with absorbent material?			
Are contamination-free areas provided for trace level analytical work?			--
Are contamination-free work areas provided for the handling of toxic materials (i.e. hood)?			
Is the air flow of the hoods periodically checked and recorded?			
Are chemical waste disposal policies/procedures adequate?			
Does the laboratory have a source of distilled/demineralized water?			
Is the conductivity of distilled/demineralized water routinely checked and recorded?			
Can the laboratory supervisor document that trace-free water is available for preparation of standards and blanks?			

III. Sample Preparation Area (Continued)

ITEM	YES	NO	COMMENT
Is the analytical balance located away from draft and areas subject to rapid temperature changes?			
Has the balance been calibrated within one year by a certified technician?			
Is the balance routinely checked with class S weights before each use and the results recorded in a logbook?			
Are the solvent storage cabinets properly vented in order to prevent possible laboratory contamination?			
Is the appropriate portion of the SOP available to the analyst at the sample preparation area?			
Are reagent grade or higher purity chemicals used to prepare standards?			
Are fresh analytical standards prepared at a frequency consistent with good QA?			
Are reference materials properly labeled with concentrations, date of preparation, and the identity of the person preparing the sample?			
Is a standards preparation and tracking logbook maintained?			
Do the analysts record bench data in a neat and accurate manner?			
Are standards stored separately from sample extracts?			

III. Sample Preparation Area (Continued)

ITEM	YES	NO	COMMENT
Is the SOP for glassware washing posted at the cleaning station?			
Is the temperature of the refrigerator/freezer recorded daily?			
Is a UV-Visible spectrophotometer operational and properly maintained?			
Is the mercury analyzer operational and well maintained (i.e. properly vented)?			
Are sufficient cyanide distillation apparatus available to routinely analyze all samples within the required holding period?			
Is the pH of the samples recorded and available for data review?			

Additional Comments

IV. Sample Analysis Instrumentation

A. ICP/DS Instrumentation

	Manufacturer	Model	Installation Date
ICP ID #			
ICP ID #			
ICP ID #			
Data System ID #			
Data System ID #			

ITEM	YES	NO	COMMENT
Are manufacturer's operating manuals readily available to the operator?			
Is there a calibration protocol available to the operator?			
Are calibrat. results kept in a permanent record?			
Is a permanent service record maintained in a logbook?			
Has the instrument been modified in any way?			
Is the instrument properly vented?			

A. ICP/DS Instrumentation (continued)

ITEM	YES	NO	COMMENT
Is the interference correction automatically performed?			
Is service maintenance by contract?			
Is preventative maintenance applied?			
Do adequate procedures exist for waste disposal from the ICP?			

SATISFACTORY?

101

Additional Comments

[illegible]

B. Atomic Absorption (AA) Spectrometer

	Manufacturer	Model	Installation Date
AA ID #			
AA ID #			
AA ID #			
Data System ID #			

ITEM	YES	NO	COMMENT
Are manufacturer's operating manuals readily available to the operator?			
Is there a calibration protocol available to the operator?			
Are calibration results kept in a permanent record?			
Is a permanent service record maintained in a logbook?			
Has the instrument been modified in any way?			
Is the instrument properly vented?			
Is the unit equipped with flameless accessory?			

V. Data Handling and Review

ITEM	YES	NO	COMMENT
Are data calculations spot-checked by a second person?			
Do records indicate corrective action that has been taken on rejected data?			
Are in-house quality control charts maintained for analysis (i.e. internal standard control charts)?			
Do QC records show corrective action when analytical results fail to meet QC criteria?			
Do supervisory personnel review the data and QC results?			

Additional Comments

[illegible]

VI. Quality Control Manual Checklist

ITEM	YES	NO	COMMENT
Does the laboratory maintain a Quality Control Manual?			
Does the manual address the important elements of a QC program, including the following:			
a. Personnel?			
b. Facilities and equipment?			
c. Operation of instruments?			
d. Documentation of procedures?			
e. Preventive maintenance?			
f. Reliability of data?			
g. Data validation?			
h. Feedback and corrective action?			
i. Instrument calibration?			

Additional Comments

VII. Summary

A. Summary Checksheet (Page 1 of 2)

ITEM	YES	NO	COMMENT
Do responses to the evaluation indicate that project and supervisory personnel are aware of QA/QC and its application to the project?			
Do project and supervisory personnel place positive emphasis on QA/QC?			f
Have responses with respect to QA/QC aspects of the project been open and direct?			
Has a cooperative attitude been displayed by all project and supervisory personnel?			
Does the organization place the proper emphasis on quality assurance?			
Have any QA/QC deficiencies been discussed before leaving?			-
Is the overall quality assurance adequate to accomplish the objectives of the project?			
Have corrective actions recommended during previous evaluations been implemented? If not provided details in Section VII.b.			

b. Additional Comments (Page 2 of 2)This image shows a single sheet of white paper with horizontal black ruling lines. The lines are evenly spaced and run across the width of the page. There are no margins, text, or other markings on the paper.

b. Additional Comments (Page 2 of 2)This image shows a single page of white paper with horizontal black ruling lines. The lines are evenly spaced and run across the width of the page. There are approximately 20 lines visible. A small dark speck is located near the top center, and another smaller one is further down towards the middle left. The paper appears slightly aged or off-white.

EXHIBIT F
SAMPLE PRESERVATION AND HOLDING TIMES

Notes

1. Polyethylene (P) or Glass (G).
2. Sample preservation should be performed immediately upon sample collection. For composite samples each aliquot should be preserved at the time of collection. When use of an automated sampler makes it impossible to preserve each aliquot, then samples may be preserved by maintaining at 4°C (+5°C) until compositing the sample splitting is completed.
3. When any sample is to be shipped by common carrier or sent through the United States Mails, it must comply with the Department of Transportation Hazardous Materials Regulations (49 CFR Part 172). The person offering such material for transportation is responsible for ensuring such compliance. For the preservation requirements of Table II, the Office of Hazardous Materials, Materials Transportation Bureau, Department of Transportation has determined that the Hazardous Materials Regulations do not apply to the following materials: Hydrochloric acid (HCL) in water solutions at concentrations of 0.04% by weight or less (pH about 1.96 or greater); Nitric acid (HNO3) in water solutions at concentrations of 0.15% by weight or less (pH about 1.62 or greater); Sulfuric acid (H2SO4) in water solutions at concentrations of 0.35% by weight or less (pH about 1.15 or greater; and Sodium hydroxide (NaOH) in water solution at concentration of 0.080% by weight or less (pH about 12.30 or less).
4. Samples should be analyzed as soon as possible after collection. The times listed are the maximum times that samples may be held before analysis and still considered valid.
5. Should only be used in the presence of residual chlorine.
6. Maximum recommended holding time is less when sulfide is present. Optionally, all samples may be tested with lead acetate paper before the pH adjustment in order to determine if sulfide is present. If sulfide is present, it can be removed by the addition of cadmium nitrate powder until a negative spot test is obtained. The sample is filtered and then NaOH is added to pH 12.
7. Samples should be filtered immediately on-site before adding preservative for dissolved metals.

EXHIBIT G

**SPECIFICATIONS FOR
CHAIN-OF-CUSTODY, DOCUMENT CONTROL,
AND STANDARD OPERATING PROCEDURES**

NOTE: The Contractor shall not deviate from the procedures described herein without the prior written approval of the Contracting Officer. Provided, that the Contracting Officer may ratify in writing such deviation and such ratification shall constitute the approval required herein.

2 DOCUMENT CONTROL PROCEDURES

The goal of the laboratory document control program is to assure that all documents for a specified case will be accounted for when the project is completed. Accountable documents used by contract laboratories shall include, but not be limited to, logbooks, chain-of-custody records, sample work sheets, bench sheets, and other documents relating to the sample or sample analyses. The following document control procedures have been established to assure that all laboratory records are assembled and stored for delivery to EPA or are available upon request from EPA prior to the delivery schedule.

2.1 Preprinted Data Sheets and Logbooks

Preprinted data sheets shall contain the name of the laboratory and be dated and signed by the analyst or individual performing the work. All documents produced by the laboratory which are directly related to the preparation and analysis of EPA samples shall become the property of the EPA and shall be placed in the case file. For that reason, all observations and results recorded by the laboratory but not on preprinted data sheets are entered into permanent laboratory logbooks. The person responsible for the work shall sign and date each entry and/or page in the logbook. When all data from a case is compiled, copies of all EPA case-related logbook entries shall be included in the documentation package. Analysts' logbook entries must be in chronological order and shall include only one case per page. Instrument run logs shall be maintained so as to enable a reconstruction of the run sequences of individual instruments.

Because the laboratory must provide copies of the instrument run logs to EPA, the laboratory may exercise the option of using only laboratory or SMO sample identification numbers in the logs for sample ID rather than government agency or commercial client names.

Using laboratory or SMO sample IDs only in the run sequences will assist the laboratory in preserving the confidentiality of commercial clients.

2.2 Error Correction Procedure

All documentation in logbooks and other documents shall be in ink. If an error is made, corrections shall be made by crossing a line through the error and entering the correct information. Changes shall be dated and initialed. No information shall be obliterated or rendered unreadable.

2.3 Consistency of Documentation

Before releasing analytical results, the laboratory shall assemble and cross-check the information on sample tags, custody records, lab bench sheets, personal and instrument logs, and other relevant data to ensure that data pertaining to each particular sample or case is consistent throughout the case file.

**SPECIFICATIONS FOR CHAIN-OF-CUSTODY, DOCUMENT CONTROL,
AND STANDARD OPERATING PROCEDURES**

1. SAMPLE CHAIN-OF-CUSTODY

A sample is physical evidence collected from a facility or from the environment. An essential part of hazardous waste investigations is that samples and data may be used as evidence in EPA enforcement proceedings. To satisfy enforcement uses of the data, the following chain-of-custody procedures have been established.

1.1 Sample Identification

To assure traceability of samples while in possession of the laboratory, a method for sample identification shall be developed and documented in laboratory Standard Operating Procedures (SOPs) (see Section 3). Each sample or sample preparation container shall be labeled with a unique number identifier (or the SMO number). This identifier shall be cross-referenced to the sample tag number and the SMO number. There shall be a written description of the method of assigning this identifier and attaching it to the sample container included in the laboratory SOPs.

1.2.1 A sample is under custody if:

1.2.1.1 It is in your actual possession,

1.2.1.2 It is in your view after being in your physical possession,

1.2.1.3 It was in your possession and then you locked or sealed it up to prevent tampering, or

1.2.1.4 It is in a secure area.

1.2.2 Upon receipt of the samples in custody, the contractor shall inspect the shipping container and sample bottles and shall document receiving information as specified in Section 3.2. The sample custodian or a designated representative shall sign and date all appropriate receiving documents at the time of receipt (i.e., EPA chain-of-custody forms, traffic reports, air-bills, etc.). The contractor shall contact SMO if documents are absent, information on receiving documents does not agree, custody seals are not intact, or the sample is not in good condition. The contractor shall document resolution of any discrepancies, and this documentation shall become a part of the permanent case file.

1.2.3 Once samples have been accepted by the laboratory, checked, and logged in, they must be maintained in accordance with custody and security requirements specified in 3.3.

2.4 Document Numbering and Inventory Procedure

In order to provide document accountability of the completed analysis records, each item in a case shall be inventoried and assigned a serialized number and identifier associating it to the case and Region.

Case # - Region - Serialized number (For example: 75-2-0240)

The number of pages of each item must be accounted for if each page is not individually numbered. All documents relevant to each case, including logbook pages, bench sheets, mass spectra, chromatograms, custody records, library search results, etc., shall be inventoried. The laboratory shall be responsible for ensuring that all documents generated are placed in the file for inventory and are delivered to EPA. Figure 1 is an example of a document inventory.

2.5 Shipping Data Packages and Case Files

The contractor shall have written procedures to document shipment of deliverables packages to the recipients. These shipments require custody seals on the containers placed such that it cannot be opened without damaging or breaking the seal. The contractor shall also document what was sent, to whom, the date, and the method (carrier) used.

3. SPECIFICATIONS FOR STANDARD OPERATING PROCEDURES

The contractor must have written standard operating procedures (SOPs) for (1) receipt of samples, (2) maintenance of custody, (3) sample storage, (4) tracking the analysis of samples, and (5) assembly of completed data.

An SOP is defined as a written narrative step-wise description of laboratory operating procedures including examples of laboratory documentation. The SOPs must accurately describe the actual procedures used in the laboratory, and copies of the written SOPs shall be available to the appropriate laboratory personnel. These procedures are necessary to ensure that analytical data produced under this contract are acceptable for use in EPA enforcement case preparation and litigation. The contractor's SOPs shall provide mechanisms and documentation to meet each of the following specifications and shall be used by EPA as the basis for laboratory evidence audits.

3.1 The contractor shall have a designated sample custodian responsible for receipt of samples and have written SOPs describing his/her duties and responsibilities.

3.2 The contractor shall have written SOPs for receiving and logging in of the samples. The procedures shall include but not be limited to documenting the following information:

- o Presence or absence of EPA chain-of-custody forms
- o Presence or absence of airbills
- o Presence or absence of traffic reports or SAS packing lists
- o Presence or absence of custody seals on shipping and/or sample containers and their condition
- o Presence or absence of sample tags
- o Sample tag ID numbers if not recorded on the chain-of-custody record(s) or packing list(s)
- o Condition of the shipping container
- o Condition of the sample bottles
- o Verification of agreement or non-agreement of information on receiving documents
- o Resolution of problems or discrepancies with the Sample Management Office

3.3 The contractor shall have written SOPs for maintenance of the security of samples after log-in and shall demonstrate security of the sample storage and laboratory areas. The SOPs shall specifically include descriptions of all storage areas for EPA samples in the laboratory. The SOPs shall include a list of authorized personnel who have access or keys to secure storage areas.

- 3.4 The contractor shall have written SOPs for tracking the work performed on any particular sample. The tracking SOP shall include the following:**
- 3.4.1 A description of the documentation used to record sample receipt, sample storage, sample transfers, sample preparations, and sample analyses.**
 - 3.4.2 A description of the documentation used to record calibration and QA/QC laboratory work.**
 - 3.4.3 Examples of the document formats and laboratory documentation used in the sample receipt, sample storage, sample transfer, and sample analyses.**
- 3.5 The contractor shall have written SOPs for organization and assembly of all documents relating to each EPA case. Documents shall be filed on a case-specific basis. The procedures must ensure that all documents including logbook pages, sample tracking records, chromatographic charts, computer printouts, raw data summaries, correspondence, and any other written documents having reference to the case are compiled in one location for submission to EPA. The system must include a document numbering and inventory procedure.**

4. HANDLING OF CONFIDENTIAL INFORMATION

A contractor conducting work under this contract may receive EPA-designated confidential information from the agency. Confidential information must be handled separately from other documentation developed under this contract. To accomplish this, the following procedures for the handling of confidential information have been established.

4.1 All confidential documents shall be under the supervision of a designated document control officer (DCO).

4.2 Confidential Information

Any samples or information received with a request of confidentiality shall be handled as "confidential." A separate locked file shall be maintained to store this information and shall be segregated from other nonconfidential information. Data generated from confidential samples shall be treated as confidential. Upon receipt of confidential information, the DCO logs these documents into a Confidential Inventory Log. The information is then made available to authorized personnel but only after it has been signed out to that person by the DCO. The documents shall be returned to the locked file at the conclusion of each working day. Confidential information may not be reproduced except upon approval by the EPA contracting officer. The DCO will enter all copies into the document control system. In addition, this information may not be disposed of except upon approval by the EPA contracting officer. The DCO shall remove and retain the cover page of any confidential information disposed of for one year and shall keep a record of the disposition in the Confidential Inventory Log.

Figure 1

232-2-0001

Case No. 232

Example

DOCUMENT INVENTORY

<u>Document Control #*</u>	<u>Document Type</u>	<u># Pages</u>
232-2-0001	Case File Document Inventory Sheet	1
232-2-0002	Chain-of-Custody Records	2
232-2-0003	Shipping Manifests	2
232-2-0004	Sample Tags	50
232-2-0005	SMO Inorganics Traffic Reports	10
232-2-0006	Inorganics Analysis Data Summary Sheets	10
232-2-0007	Analysts' Notebook Pages	14
232-2-0008	ICAP and AA Instrument Logbook Pages	12
etc.	etc.	etc.

*This number is to be recorded on each set of documents.

3.10 QUALITY CONTROL PROCEDURES

3.10.1 Laboratory Quality Control Checks

Procedures for laboratory quality control checks to be utilized by Kemron are documented in Section 3.9.

3.10.2 Field Quality Control Checks

Quality control samples generated by G&M will include the collection of field replicates, the preparation of field blanks, and the use of trip blanks. To assess laboratory performance, replicates will be collected in the field and sent to the analytical laboratory at a frequency of about 10 percent of the sample set. The anticipated number of quality control samples to be generated during Phase I of the RI is summarized in Table 3.10-1

Trip blanks will be shipped along with water samples and will be analyzed at the same time as all other samples. Trip blanks will be utilized at a rate of one sample per shipment.

Field blanks will be prepared using rinse water from the ground-water sampling equipment, and will be analyzed to determine if the sampling procedures may be biasing the data.

GERAGHTY & MILLER, INC

Section No. 3.10
Revision No. 1
Date: 6-17-87
Page 2 of 2

Field blanks will be prepared and submitted at a rate of one per day. Procedures for collecting these samples are discussed in Section 3.6.5.

TABLE 3.10-1

SUMMARY OF FIELD GENERATED QUALITY CONTROL SAMPLES

<u>Sampling Event</u>	<u>Sample Type</u>	<u>Actual Samples</u>	<u>Replicates</u>	<u>Field Blanks</u>	<u>Trip Blanks</u>	<u>Total Samples Generated</u>
Ground-water and Seep Sampling	Water	57-60	6	10	5-10	78-86
Pond solids Sampling	Pond Solids	45	5	-	-	50
Former Potliner Storage Area Characterization	Soils ¹	120	12	-	-	132
	Soils ²	20-40	2-4	-	-	22-44
River Sediment Sampling	Sediment & Water	6	1	-	-	7
Carbon Runoff and Deposition Area Characterization	Carbon Material	6	1	-	-	7
	Soil	6	1	-	-	7

¹ Soil samples to be analyzed for six inorganic indicator parameters

² Soil samples to be analyzed for complete CLP list

3.11 PERFORMANCE AND SYSTEM AUDITS

To verify compliance with the stated QA/QC objectives , (Section 3.4.), the G&M QA/QC Officer will periodically (e.g., during major sampling events) perform audits of project activities. These audits will consist, where appropriate, of an evaluation of quality assurance/quality control procedures and the effectiveness of their implementation, an evaluation of work areas and activities, and a review of project documentation. Audits will be conducted using the written checklists provided in Figures 3.11-1 and 3.11-2. Results will be documented and reported to the G&M Project Director and G&M Project Manager.

Audits may address the following areas:

- Subcontractor performance
- Field operations and records
- Identification and control of samples
- Numerical analyses
- Transmittal of information
- Document control and retention
- Health and Safety procedures

FIGURE 3.11-1

SYSTEM AUDIT CHECKLIST

PROJECT OFFICE

Project No. : _____

Client: _____

Location _____

Date: _____

YESNOProject Management

- | | | |
|---|---|--|
| — | — | • Were appropriate project personnel selected and do they have adequate skills/training (Health and Safety equipment, etc.)? |
| — | — | • Was a general project briefing held for participating personnel? |
| — | — | • Was a task-specific briefing held prior to implementing current field activities? |

Data Management

- | | | |
|---|---|--|
| — | — | • Is the document control system being adhered to? |
| — | — | • Are all documents accounted for and secure? |

Field Work Set-up

- | | | |
|---|---|--|
| — | — | • Is there a list of accountable field documents? |
| — | — | • Has coordination been established with contractors and laboratories? |

FIGURE 3.11-1 (cont.)

<u>YES</u>	<u>NO</u>	
		<u>Data Review and Reporting</u>
<u> </u>	<u> </u>	• Have data review responsibilities been assigned?
<u> </u>	<u> </u>	• Has a data base been established and validated?
<u> </u>	<u> </u>	• Have reporting requirements been reviewed?

Comments:

Auditor Name: _____

Auditor Signature: _____

FIGURE 3.11-2
SYSTEM AUDIT CHECKLIST
FIELD OPERATIONS

Project No: _____

Client: _____

Location: _____

Date: _____

Field Personnel:

<u>YES</u>	<u>NO</u>	
___	___	• Is there a set of accountable field documents checked out to the on-site personnel?
___	___	• Is the Health and Safety Plan being adhered to?
___	___	• Is safety and sampling equipment available and suitable to tasks?
___	___	• Are checklists, log-books, and other field data forms up-to-date and properly filled out?
___	___	• Are field equipment calibration logs maintained and any corrective action noted?
___	___	• Are samples collected according to project plan or per direction of on-site coordinator?
___	___	• Are samples collected in appropriate containers and preserved as specified in Project Plan?
___	___	• Are samples properly identified (labeled)?
___	___	• Are blanks and replicate samples properly identified and documented in log books?
___	___	• Is proper chain-of-custody being maintained?

FIGURE 3.11-2 (cont.)

<u>YES</u>	<u>NO</u>	
<u> </u>	<u> </u>	• Are blanks and replicate samples properly identified and documented in log books?
<u> </u>	<u> </u>	• Is proper chain-of-custody being maintained?
<u> </u>	<u> </u>	• Are all documents accounted for?

Comments:

Auditor Name: _____

Auditor Signature: _____

Auditing of field operations will include examination of: implementation of approved work procedures; calibration and operation of equipment; labeling, packaging, storage, and shipping of samples; and documentation of subcontractor performance. The records of all field activities shall be reviewed to verify that field-related operations were performed according to appropriate project procedures. Items reviewed will include, but are not limited to: field equipment calibration logs, daily field activity logs, all field data logs, and checklists resulting from field operations.

During an audit and upon its completion, the auditor will discuss the findings with the individuals audited and cite changes to be initiated. Minor deficiencies that can be resolved to the satisfaction of the auditor during an audit are not required to be cited as requiring change. All findings that are not resolved during the course of the audit and that require substantive changes will be noted on the audit checklists.

Following completion of an audit, the auditor will prepare a summary report of findings to be submitted to the G&M Project Director and the G&M Project Manager. This report will serve to notify management of the audit results and may also be sent to individuals contacted during the audit and the management of any affected subcontractor.

GERAGHTY & MILLER, INC.

Section No. 3.11
Revision No. 2
Date: 9-21-87
Page 7 of 7

In addition to the performance and system audits to be conducted by G&M, the U.S. EPA Region V Central Regional Laboratory will perform external performance and system audits of the laboratories supplying the analytical services^f for the Phase I RI.

3.12 PREVENTIVE MAINTENANCE

Preventive maintenance on field equipment will be performed in accordance with procedures supplied by the manufacturer. The manufacturer's operating and maintenance manuals will be kept on site and reviewed by personnel involved in equipment use. Frequent calibration procedures, as outlined in Section 3.8. will be used as a means of determining the need for equipment maintenance.

The maintenance of laboratory equipment will be performed by the laboratory according to specified procedures outlined in Reference 6.

3.13 SPECIFIC ROUTINE PROCEDURES USED TO ASSESS DATA PRECISION, ACCURACY, AND COMPLETENESS

All data generated in this investigation will be assessed for its representativeness, accuracy, and precision. The completeness of the data will be determined by comparing the acquired data to the stated project objectives to see that the objectives are being met. The procedures utilized by the analyzing laboratories to determine data precision, accuracy, and completeness are described in Section 3.9. Additional checks on method precision will be performed using similar methods on field collected replicate samples. Accuracy will be assessed using laboratory spiked samples and laboratory field blanks.

The representativeness of the data will be assessed by first determining if the proper procedures and protocols were followed during the collection of the samples from which the data were generated. Any non-adherence to the procedures and protocols shall be evaluated to determine its potential effect, if any, on the data. Also, the data validation package supplied by the laboratory (as required under the Contract laboratory Program) for each sample analysis will be reviewed to determine if there may be any laboratory-related sources of error in data.

Precision and accuracy will be assessed using QC samples as outlined in Section 3.10. Precision will be examined using replicate samples and accuracy by using blanks and spiked

This methodology is summarized in Section 3.9.

3.14 CORRECTIVE ACTION

If the periodic quality-control audits detect unacceptable conditions or data, the G&M Project Director, G&M QA/QC Officer, and G&M Project Manager are responsible for developing and initiating appropriate changes or modifications. The condition or problem will be specifically identified, recorded in the appropriate field log or project file, investigated, and the cause determined. Then, changes or modifications will be initiated to eliminate the problem. These may include:

- Re-analyzing samples if holding time and sample volume permit,
- Resampling and re-analyzing,
- Evaluating and amending sampling and/or analytical procedures,
- Accepting data, while documenting a level of uncertainty.

Upon implementation of changes or modifications, their effectiveness will be established and elimination of the problem verified. Details regarding the changes or modifications implemented and the results will be documented and retained in the project file.

3.15 QA REPORTS TO MANAGEMENT

On a regular basis, the G&M QA/QC Officer will review all aspects of the implementation of this QAPP and prepare a summary report to the G&M Project Manager and G&M Project Director. Reviews will be performed at the completion of each field activity and reports will be completed at this time. These reports will include:

- Assessments of measurement data accuracy, precision, and completeness,
- Results of performance, systems, data, and instrument audits, and
- Any changes or modifications which need to be taken or are to be taken.

Any significant QA problems will be reported and identified, and options for changing or modifying the program can be discussed.

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION V

DATE: December 24, 1987

SUBJECT: Approval of Quality Assurance Project Plan for Remedial Investigation/
Feasibility Study activity at the Ormet Corporation site, Ohio

FROM: *James D. Adams, Jr. for*
Andrea Jirka, Chief
Data Quality Assurance Branch

TO: Norman Niedergang, Chief
CERCLA Enforcement Section

Attention: Rhonda McBride, RPM

We are returning a copy of an approved quality Assurance Project Plan (QAPP) for Remedial Investigation/Feasibility Study activity at the Ormet Corporation site, Ohio, which our QAS office received on December 18, 1987 (QAS#485). The original signature page is included. Please have the Remedial Project Manager provide final sign off. We have retained a copy of this subject QAPP for our records.

cc: K. Chiu, ERRB